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(12) # EUROPEAN PATENT APPLICATION

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(54) Optical device including birefringent polymer.

(57) Optical devices including a molecularly oriented highly birefringent polymer are disclosed. The devices include molecularly oriented polymers comprising recurring units (L) which exhibit a distribution of high electron density about the long axes (X) of the polymer and the recurring units (L) thereof. Transparent birefringent polymers comprising a plurality of recurring units (L) having a substantially cylindrical distribution of electron density about the long axis (X) of such units and the chain-extended polymers are included in optical devices and articles. The polymers exhibit high birefringence and simulate in a polymer the optical properties of a uniaxial crystal.
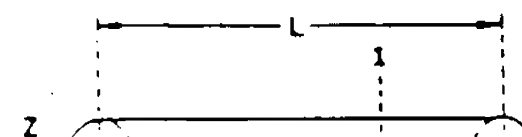
Specification

BACKGROUND OF THE INVENTION

This invention relates to an optical device or article. More
particularly, it relates to such an article or device in-
cluding a molecularly oriented highly birefringent poly-
meric material.

Materials having a birefringent character have been variously
applied in connection with the construction of filter and
other optical devices. Frequently, a birefringent element
utilized in an optical filter or other device will comprise
a plate made from a monocrystalline form of birefringent
material. Single crystals are expensive materials and are not
readily formed to the desired shape or conformation required
in particular applications. The size to which crystals can be
grown represents an additional limitation on the utilization
of such materials in optical devices.

Optical devices including a birefringent material in the
form of a polymeric layer, such as may be formed by the uni-
directional stretching of a suitable polymeric material, have
also been described. Thus, light-polarizing devices utilizing
a polymeric birefringent layer have been described in U.S.
Patent 3,213,753 (issued October 26, 1965 to H.G. Rogers).
Optical devices including polymeric birefringent materials
have also been set forth, for example, in U.S. patent
3,506,333 (issued April 14, 1970 to E.H. Land) and in U.S.
Patent 3,610,729 (issued October 15, 1971 to H.G. Rogers).
Frequently, the efficiency of an optical filter, polarizing

ences in refractive index between a birefringent material and
adjacent or contiguous layers. In general, such net differ-
ences will be maximized where the birefringent material is
similarly birefringent and correspondingly large differences
in refraction indices of contiguous layers will be unattainable

1 where birefringent polymeric materials otherwise suited to
application in an optical device tend to exhibit either low
or only marginal birefringent character. Accordingly,
optical devices including polymeric layers or elements ex-
hibiting a highly birefringent character will be of
5 particular interest for optical applications and enhanced
efficiency.

SUMMARY OF THE INVENTION

10 The present invention provides an optical device or article
which includes a molecularly oriented and optically uni-
axial highly birefringent polymer. The polymer comprises
repeating molecular units exhibiting high electron density
substantially cylindrically distributed about the long axis
15 of the polymer and the repeating units thereof. It has been
found that the birefringent character of a polymer is
importantly releated to the molecular configuration or
structure of the repeating units of the polymer and to the
distribution of electron density about the long axis of the
20 polymer and the repeating units thereof. Thus, it has been
found that the provision, in a transparent polymeric
material comprising a plurality of repeating units in
chain-extended relationship, of a substantially cylindrical
distribution of electron density about the long axis of the
25 polymer permits the realization of high birefringence and
the simulation in a polymeric material of optical
properties of a uniaxial crystal.

birefringent polymer, said highly birefringent polymer
comprising repeating molecular units exhibiting high
electron density substantially cylindrically distributed
about the long axis of the polymer and the repeating units
35 thereof, said highly birefringent polymer being optically

uniaxial exhibiting only two indices of refraction. It has
been found that birefringence of a polymeric material useful
in articles or devices of the present invention exhibit bi-
refingence in relation to the molecular configuration of the
repeating molecular units and the cylindrical or ellipsoidal
electron density distribution about the axes of the polymer
and the recurring units thereof, said birefringence being
in relation to said molecular configuration and said
electron density distribution according to a dimensionless
geometric index G represented by the relationship

$$G = 0.222 \times E \times \frac{L}{D}$$

where in E is a dimensionless eccentricity factor defined
by the relationship

$$E = \frac{1 + e_L}{1 + e_T}$$

where e_L is the longitudinal eccentricity of the polarizab-
ility of the repeating molecular unit and e_T is the trans-
verse eccentricity of the electron polarizability of the
repeating molecular unit, L is the length of the repeating
molecular unit along the main axis thereof and D is the mean
diameter of the repeating molecular unit.

A preferred article of the present invention is a multi-
layer light-transmitting device including at least one
additional transparent layer having an index of refraction

birefringent material; said at least one additional trans-
parent layer, when a layer of birefringent material, having

the index of refraction of said layer of transparent mate-

cularly oriented highly birefringent polymeric material and having a molecular orientation substantially perpendicular to the molecular orientation of said molecularly oriented hightly birefringent polymeric material.

THE DRAWINGS

Fig. 1   is a geometric representation of molecular dimensions of a repeat unit of a polymeric material.

Fig. 2   is a cross-sectional view along the line 1-1 of Fig. 1.

Fig. 3   is a vectorial representation of bond and group polarizabilities of a repeat unit of a polymeric material.

Figs. 4a and 4b show, respectively, ellipsoidal and circular cross-sectional distribution of electron density about the long axis of a recurring unit of a polymeric material.

Fig. 5   is a diagrammatic fragmentary edge view of a light-transmitting device of the present invention illustrating the transmission of light rays therethrough.

Fig. 6   is a diagrammatic side view of an automotive vehicle headlamp which includes a light-polarizing filter of the invention.

embodiment of the present invention showing incident light thereon being partly transmitted and partly reflected as separate linearly polarized

1   Fig. 8   is a diagrammatic side view of an optical beam-
splitter device including a birefringent poly-
meric material.

DETAILED DESCRIPTION OF THE INVENTION

5

As indicated hereinbefore, the present invention provides
an optical device including a transparent, molecularly
oriented and highly birefringent polymeric material. The
birefringent polymeric material of the devices of the in-

10 vention comprises repeat molecular units which exhibit
high electron density substantially cylindrcally distributed
about the long axes of the polymer and the repeat units
thereof. The polymeric material, comprised of repeating
units of molecular structure such as to provide a sub-

15 stantially cylindrical distribution of electron density
about the long axis or backbone of the polymer, exhibits
optical anisotropy or birefringence in accordance with the
relationship

20
$$G = 0.222 \left(\frac{1 + e_L}{1 + e_T} \right) \frac{L}{D}$$

where G represents the geometric index of a repeating unit;
e_L is the longitudinal eccentricity of the electron polar-

25 izability of the repeating molecular unit; e_T is the trans-
verse eccentricity; L is the length of the repeating unit
along the main axis thereof; and D is the mean diameter of
the repeating molecular unit. The contribution to bire-

be better understood by reference or the drawings hereof.

In Fig. 1 is shown a geometrical presentation of a

35 material. Each repeating unit may thus be visualized as a

1 repeating rod-like segment of finite length L and of a
generally cylindrical configuration. Birefringence has been
found to be importantly related to the molecular structure
of the repeating units of the polymer in accordance with
the relationship of geometric index G, set forth herein-
5 before. A highly birefringent polymeric material useful in
the optical devices hereof will thus comprise a plurality
of molecular units in chain-extended relationship, each
unit having a length L, shown in Fig. 1. The long axis X of
each repeating unit forms, in the chain-extended polymer,
10 the long axis or backbone. Each axis in Fig. 1 forms a
right angle with respect to any other axis. The mean dia-
meter D, set forth in the geometric index G, is determined
for each repeating unit by the expression

15 $D = \frac{Y + Z}{2}$. In Fig. 2 is shown along line 1-1 of Fig. 1, a
cross-sectional view. The shown Y and Z axes are at right
angles to one another, the X axis comprising the axis of
the cylinder extending in a direction normal to the plane
of the paper.

20

In addition to a rigid rod-like geometry in a polymeric
material as the result of an end-to-end combination of
repeating units, the electron density distributed around
the long axis of the polymer, variously treated as a
25 cylindrical or ellipsoidal distribution, is believed to
comprise a major contributing factor to optical anisotropy
or birefringence. High electron density substantially
cylindrically distributed around the long axis of a polymer

orthogonal, biphenyl groups. An orthogonal...
between adjacent phenylene rings can be nearly attained by
the placement of substituents with large steric effects on
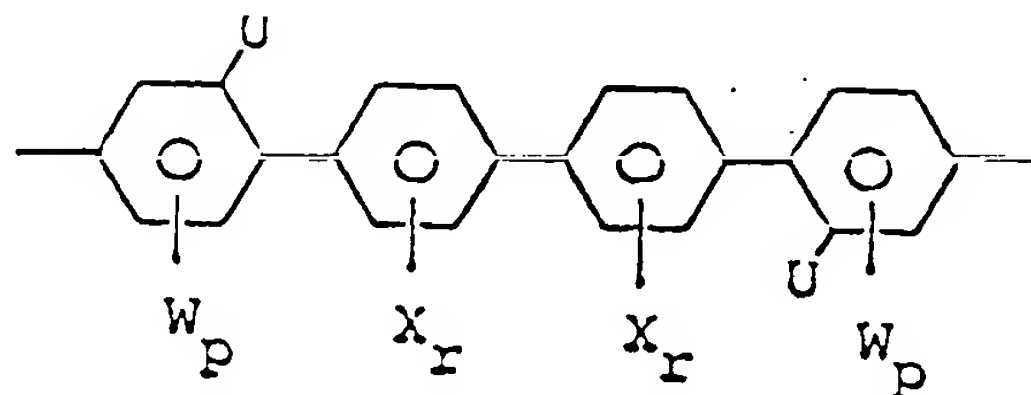inter-ring bond. In Fig. 3 is shown a vectorial represent-
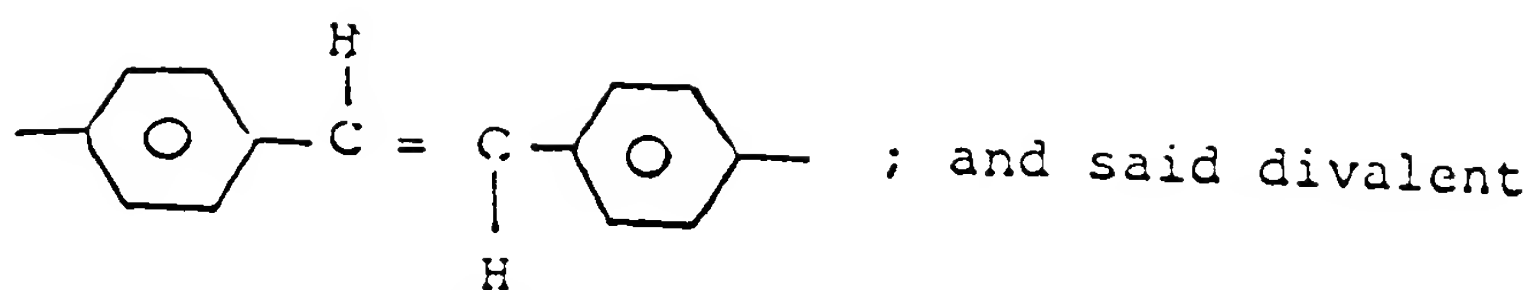
; and said divalent

radical B is a substituted quaterphenylene radical having
the formula

wherein each U is a substituent other than hydrogen, each W
is hydrogen or a substituent other than hydrogen, each p is
an integer from 1 to 3, each X is hydrogen or a substituent
other than hydrogen and each r is an integer from 1 to 4,
said U, W_p and X_r substitution being sufficient to provide
said radical with a non-coplanar molecular configuration.

24. A device according to claims 22 or 23 each of U and
X_1 in said formula of radical B is a substituent selected
from the group consisting of halogen, nitro, alkoxy and
trifluoromethyl.

25. A multilayer light-transmitting device comprising, in
assembled bonded relation: a layer of transparent molecular-
ly oriented highly birefringent polymer according to any
of the preceding claims; said multilayer light-transmitting
device including at least one additional transparent

and comprising isotropic or birefringent material; said at
least one additional transparent layer, when a layer of

1 thereof substantially different from one index of refract-
ion of said layer of transparent molecularly oriented
highly birefringent polymer and having a molecular orient-
ation substantially perpendicular to the molecular orient-
ation of said molecularly oriented highly birefringent

5 polymer.

26. A multilayer light-transmitting device according to
claim 25 wherein said layer of transparent molecularly
oriented highly birefringent polymer is bonded to a trans-

10 parent layer having an index of refraction substantially
matching one index of refraction of said transparent
molecularly oriented highly birefringent polymer.

27. A multilayer light-transmitting device according to

15 claim 25 wherein said layer of transparent molecularly
oriented highly birefringent polymer is bonded between two
transparent layers, one transparent layer having in index
of refraction substantially matching the lower index of
refraction of said transparent molecularly oriented highly

20 birefringent polymer.

28. A multilayer light-transmitting device according to
claim 27 wherein one of said two transparent layers has an
index of refraction substantially matching the lower index

25 of refraction of said transparent molecularly oriented
highly birefringent polymeric material and the second of
said two transparent layers has an index of refraction
substantially matching the higher index of refraction of

29. A multilayer light-transmitting device according to
claim 25 comprising an alternating arrangement of a
plurality of layers of said transparent molecularly oriented

35 birefringent polymer and a plurality of said additional

index value of 1.2 or higher. Experimentally determined birefringence values for polymeric materials have been found to correlate with calculated geometric indices. For example, a geometric index of 1.20 was calculated for the recurring structural unit of the following polymer:
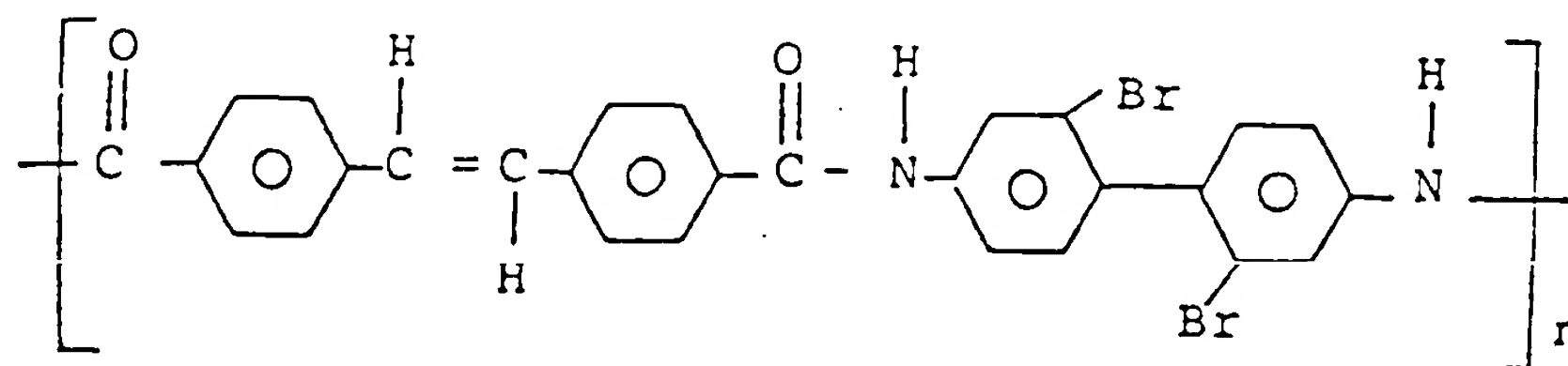

Theoretical maximum birefringence (Δn_{max}) was obtained by plotting the orientation function for the polymer (calculated from infrared dichroism) against the measured birefringence of the polymer and extrapolating to 100 % orientation. A Δn_{max} value of 1.20 was obtained. In like manner, a correlation of geometric index G of 1.18 and Δn_{max} of 0.98 was obtained in connection with the following polymer comprising the shown recurring unit:
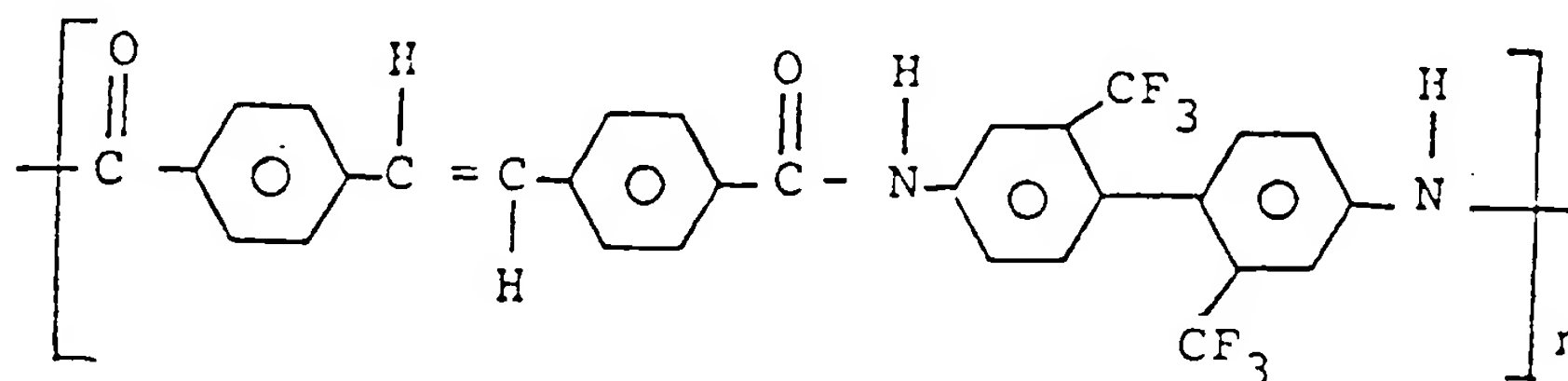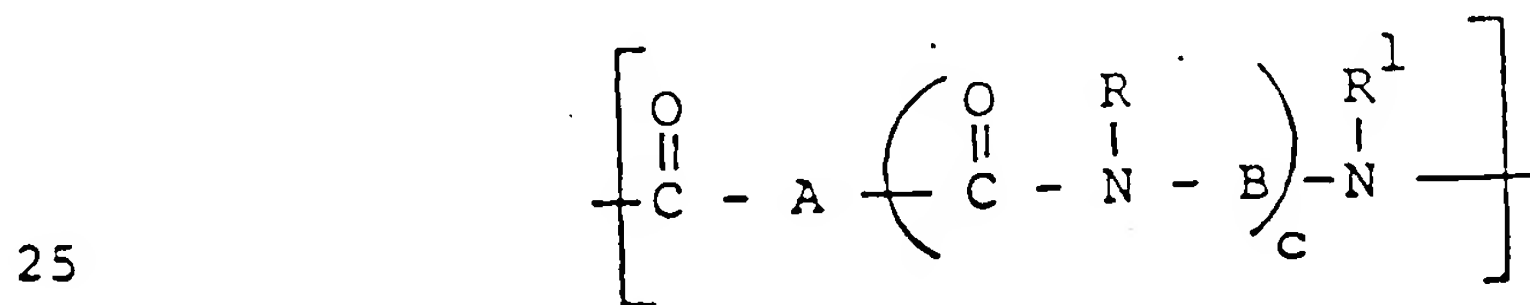

A number of polymeric materials comprising recurring units having a geometric index as hereinbefore defined of about 0.5 or higher can be suitably employed in oriented form as a birefringent polymeric material in an optical device of

...tibonded p-phenylene moieties of non-coplanar molecular configuration are especially suited herein and are generally characterized by geometric index values of ...

1 high geometric index G and high birefringence are certain
   polyamide materials including recurring units comprised,
   for example, of interbonded aromatic rings where the
   aromatic rings are in twisted relation to one another, i.e.,
   where the aromatic rings are in a non-coplanar molecular
5 configuration with respect to each other or, preferably, in
   mutually orthogonal planes. It has been found that the
   presence of substituent moieties on interbonded aromatic
   radicals, of type and position such as to effect a non-
   coplanar molecular configuration with respect to the inter-
10 bonded aromatic radicals, provides a recurring unit having
   a high geometric index. The condition of non-coplanarity
   among aromatic rings in a recurring unit, or presence in
   such units of rings in "twisted" configuration relative to
   one another has been found to be importantly related to
15 high birefringence in the rigid rod-like oriented polymers
   resulting from the end-to-end joining of such recurring
   units.

   Among polyamide materials suited to application as highly
20 birefringent layers in the devices of the invention are
   polyamides comprising repeating units of the formula

25

$$\left[\begin{matrix} O \\ \| \\ C \end{matrix} - A \left(\begin{matrix} O \\ \| \\ C \end{matrix} - \begin{matrix} R \\ | \\ N \end{matrix} - B \right)_c - \begin{matrix} R^1 \\ | \\ N \end{matrix} \right]$$

30 each hydrogen, alkyl (e.g.,
   phenyl, naphthyl), alkaryl (e.g., tolyl), aralkyl (e.g.,
   benzyl); c is zero or one; and wherein, when c is one, at

   the group consisting of:

35

(1) a divalent substituted biphenyl radical
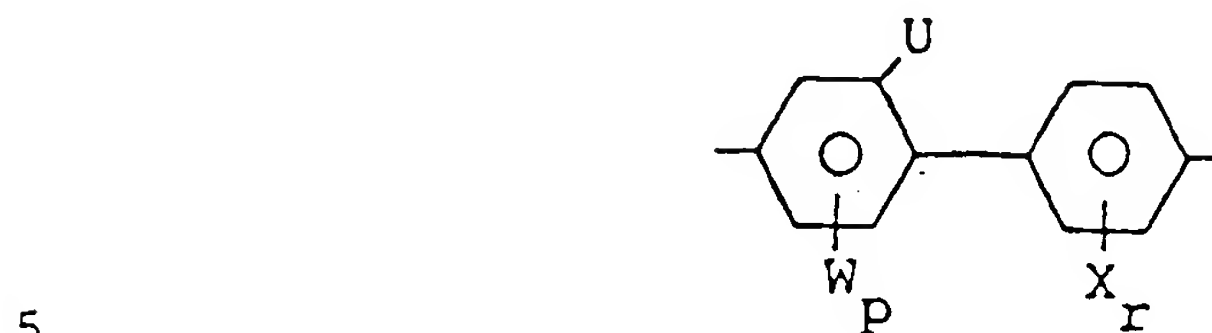
where U is a substituent other than hydrogen, each W is hydrogen or a substituent other than hydrogen, p is an integer from 1 to 3, each X is hydrogen or a substituent other than hydrogen and r is an integer from 1 to 4, said U, Wp and Xr substitution being sufficient to provide said radical with a non-coplanar molecular configuration; and

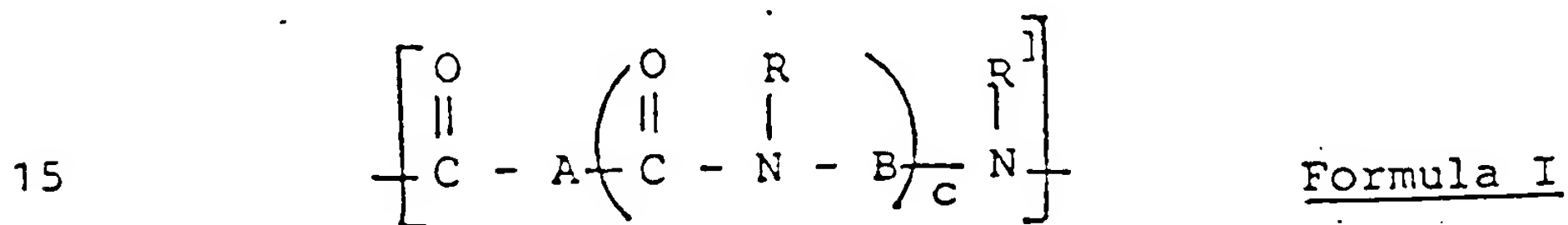(2) a divalent substituted stilbene radical
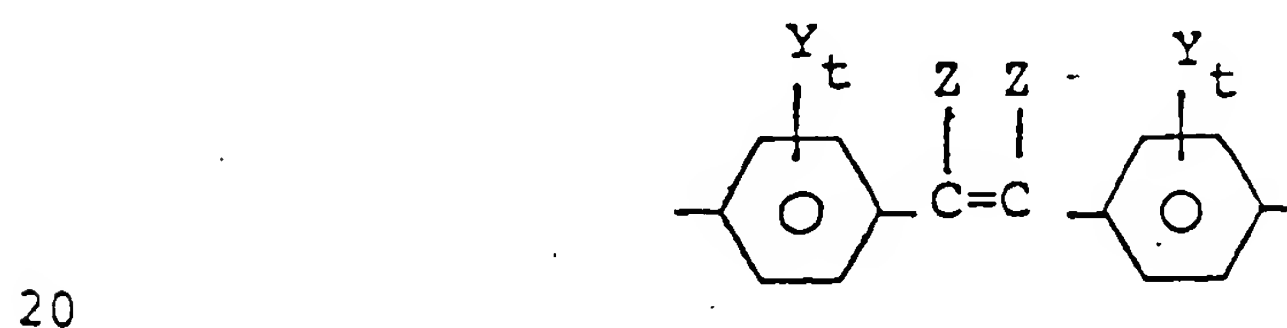
where each of Y and Z is hydrogen or a substituent other than hydrogen and each t is an integer from 1 to 4, with the proviso that when each said Z is hydrogen, at least one said Y substituent is a substituent other than hydrogen positioned on the corresponding nucleus ortho with respect to the
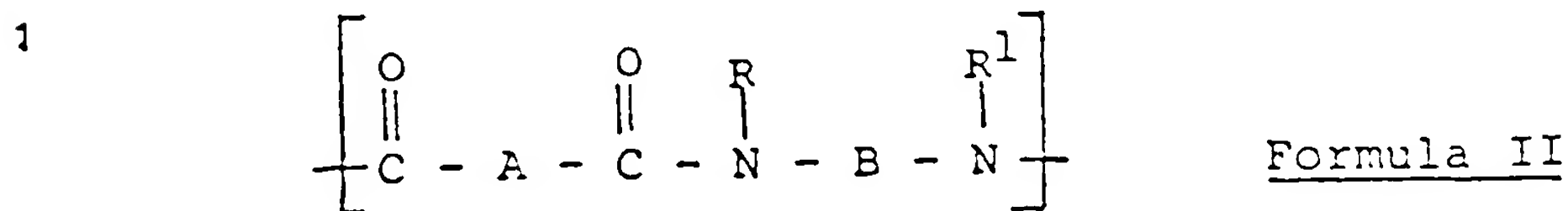
coplanar molecular configuration;

as hereinbefore defined.

1 As used herein, substitution sufficient to provide a radical with a non-coplanar molecular configuration refers to substitution of type and position effective to confer to the interbonded aromatic radical thereof a non-coplanar molecular configuration such that the value of the geo-

5 metric index, as hereinbefore defined, is about 0.5 or higher. Preferably, the nature of such substitution will be sufficient to provide a G value of 1.0 or higher, and most preferably, 1.2 or higher.

10 As described hereinbefore, birefringent polyamides useful in devices of the present invention include those comprising recurring units of the formula

$$\left[\begin{matrix} O \\ \| \\ C \end{matrix} - A \left(\begin{matrix} O \\ \| \\ C \end{matrix} - \begin{matrix} R \\ | \\ N \end{matrix} - B \right)_c \begin{matrix} R^1 \\ | \\ N \end{matrix} \right]$$ Formula I

15

wherein c is zero or one and wherein A (when c is zero) or at least one of A and B (when c is one) comprises a sub-stituted divalent biphenyl radical or a sub-

20 stituted divalent stilbene radical. Thus, when c is zero, divalent radical A comprises a substituted biphenylene radical having a non-coplanar molecular configuration or a substituted divalent stilbene radical of non-coplanar molec-ular configuration. Similarly, when c is the integer one,

25 one or both of divalent radicals A and B comprises such sub-stituted biphenylene or substituted stilbene radicals. It is preferred from the standpoint of ease of preparation that each of R and R^1 be hydrogen, although each of R and

From inspection of the general formula descriptive of recurring units of the polyamides of formula I, it will be appreciated that polyamides comprising

- 13 -

1
$$\left[\begin{array}{c} O \\ \parallel \\ C \end{array} - A - \begin{array}{c} O \\ \parallel \\ C \end{array} - \begin{array}{c} R \\ | \\ N \end{array} - B - \begin{array}{c} R^1 \\ | \\ N \end{array} \right]$$ Formula II

5 In such recurring units, at least one of divalent radicals A and B will comprise a substituted biphenylene or substituted stilbene radical of non-coplanar, molecular configuration conforming to the formulae

10
    ;   Formula III

15   or
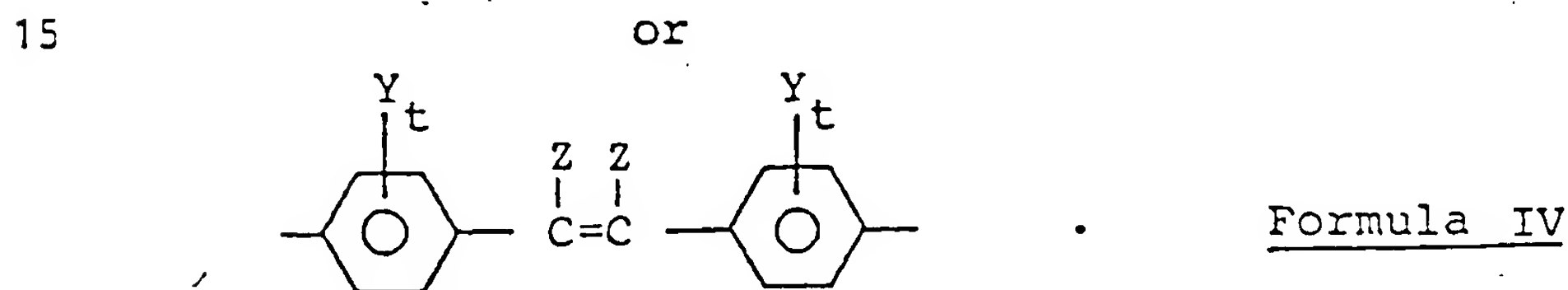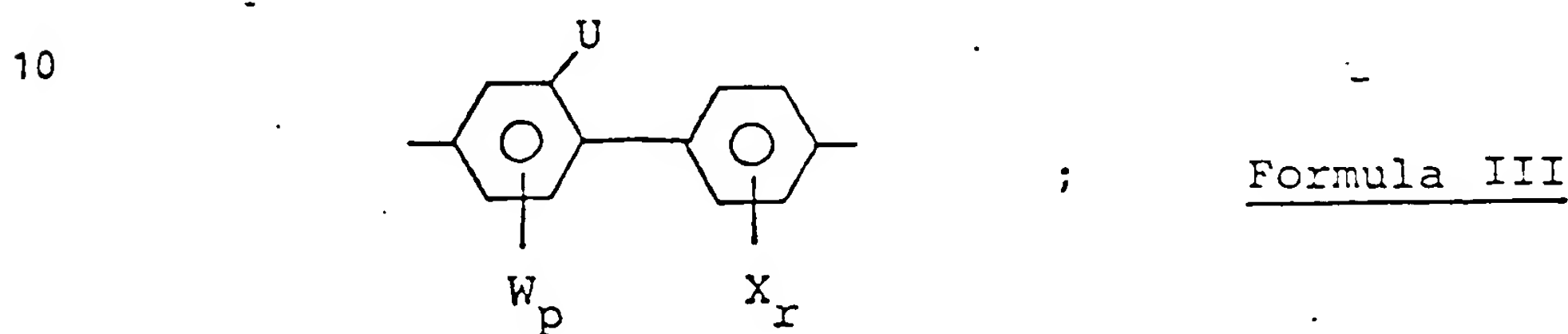
    .   Formula IV

20

Where only one of said A and B radicals is a substituted biphenylene or substituted stilbene radical conforming to the radicals represented by the structures of Formulas III and IV, the remaining A or B radical can comprise any of a
25 variety of divalent radicals so long as the birefringent properties of the polyamide material are not effectively negated. In general, where only one of the A and B radicals

eccentricity to the recurring unit. Similarly, where one of radicals A or B is a radical which confers transverse

35 itudinal eccentricity such that the recurring unit of the

1   polymer exhibits a high geometric index. Suitable divalent
radicals include, for example, unsubstituted biphenylene
or stilbene radicals; phenylene; trans-vinylene; or
ethynylene. Also suitable are polyunsaturated divalent
radicals conforming to the formula

5

$$:\left(\begin{matrix} & E \\ & | \\ C = C \\ | \\ D \end{matrix}\right)_n$$
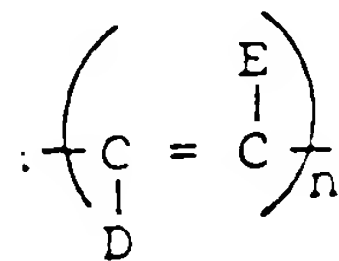
10   where n is an integer of at least two (e.g., two or three)
and each of D and E is hydrogen or alkyl (e.g., methyl) and
inclusive of such polyunsaturated divalent radicals as

trans-trans-1,4-butadienylene, i.e., $-\overset{\underset{\displaystyle H}{|}}{C}=\overset{\underset{\displaystyle H}{|}}{C}-\overset{\underset{\displaystyle H}{|}}{C}=\overset{\underset{\displaystyle H}{|}}{C}-$; and 1,4-

15

dimethyl-trans-trans-1,3-butadienylene, i.e., $-\overset{\overset{\displaystyle CH_3}{|}}{C}=\overset{\overset{\displaystyle H}{|}}{C}-\overset{\overset{\displaystyle H}{|}}{C}=\overset{\underset{\displaystyle CH_3}{|}}{C}-.$

It will appreciated that compounds containing amino groups
20   directly attached to carbon atoms having linear unsaturated
radicals are not stable and that, accordingly, the afore-
said vinylene, ethynylene and butadienylene radicals
cannot serve as B radicals in the recurring units repre-
sented by the structure of Formula II.

25

In general, from the standpoint of maximized birefringent
properties, it will be preferred that each of radicals A
and B comprise a divalent radical exhibiting a non-coplanar
molecular configuration and conforming to the structures

affect the ability to readily orient the polymer
as by extrusion, stretching or the like. Accordingly, where
the ability of a polyamide material to be oriented is

1 each of radicals A and B of non-coplanar molecular configur-
ation and conforming to the structures of Formulas III or
IV, it will be preferred that only one of such radicals A
and B of the polyamide material conform to the structure
of Formulas III or IV.

5

In the case of radicals A and/or B of the recurring type
represented by Formula III, U will comprise a substituent
other than hydrogen; W will be either hydrogen or a sub-
stituent other than hydrogen; and p will be an integer of
10 from 1 to 3. In the case of such radicals, X will be
hydrogen or a substituent other than hydrogen and r will be
an integer of from 1 to 4. It will be appreciated from the
nature of U, W, p, X and r, as set forth, that at least
one aromatic nucleus of the biphenylene radical represented
15 by Formula III will be substituted by a moiety other than
hydrogen and that such substituent, U, will be positioned
in an ortho relationship to the bridging carbon atoms of
the biphenylene nuclei. Preferably, each aromatic nucleus
of the biphenylene radical of Formula III will contain a
20 substituent other than hydrogen positioned in an ortho
relationship to the bridging carbon atoms of the bi-
phenylene radical of Formula III and in this case, the
divalent radical will have the following formula

25
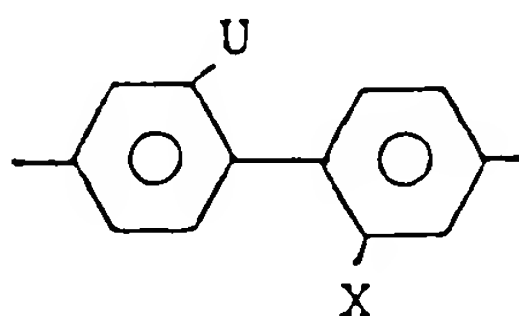
Formula V

hydrogen.

The nature and positioning of substituents U, W and X of
the polymer are chosen

35 consistent with the provision of a biphenylene radical

1   having a non-coplanar molecular configuration. While
applicants do not wish to be bound by precise theory or
mechanism in explanation of the highly birefringent
character observed in oriented polymers comprising recurring
units of high geometric index, it is believed that the non-

5   coplanar character conferred or promoted by the presence in
a polymer of such recurring units provides a distribution
of high electron density cylindrically about the long axis
of the polymer. This distribution is believed to be
importantly related to unusually high birefringence .

10 observed in such polymers.

The nature of substituency, U, Wp and Xr should be such as
to provide the biphenylene radical of formula III with a
non-coplanar molecular configuration referred to herein-

15 before. Such configuration will in part be determined by
the positioning and size of non-hydrogen substituents on the
aromatic nuclei of the biphenylene radical and upon the
number of such substituents on such aromatic nuclei. For
example, where the biphenylene radical contains a single

20 non-hydrogen substituent, i.e., substituent U, the nature
and, in particular the size of such U substituent, should
be such as to provide the desired non-coplanar molecular
configuration. Suitable U substituents herein include
halogen (e.g., fluoro, chloro, bromo, iodo); nitro; alkyl

25 (e.g., methyl, ethyl); alkoxy (e.g., methoxy); substituted-
alkyl (e.g., trifluoromethyl or hydroxymethyl); cyano;
hydroxy; thioalkyl (e.g., thiomethyl); carboxy; sulfonic
acid esters; sulfinic acid esters; carboxyamide; sulfon-
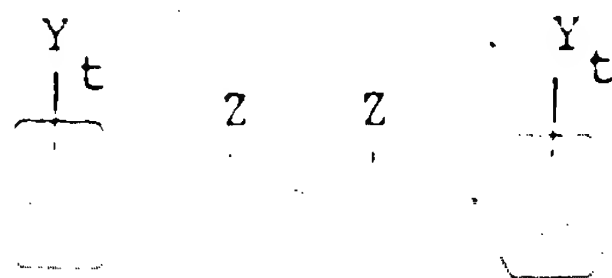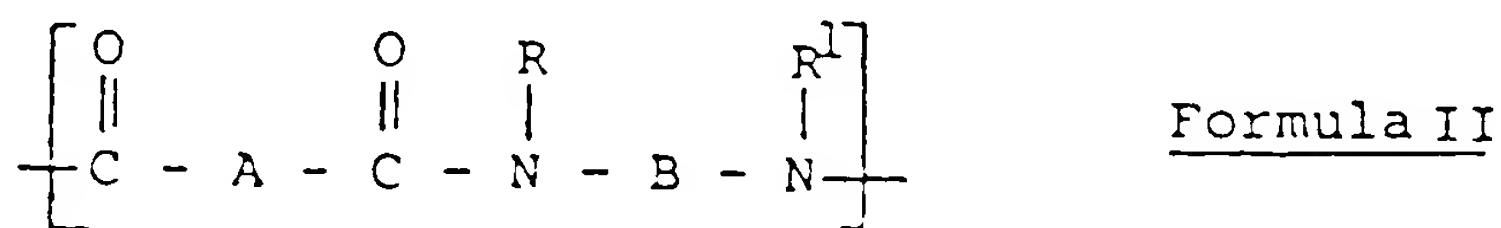amide; amino; and carbonyl. Substituent X can comprise

will comprise a substituent other than hydrogen and
substituent W can comprise hydrogen or a substituent other
than hydrogen set forth in connection with substituents

integer 3.

1 Preferred polyamides herein are the polyamides comprising
recurring units having the biphenylene radical of
Formula V, i.e.,

5

Formula V
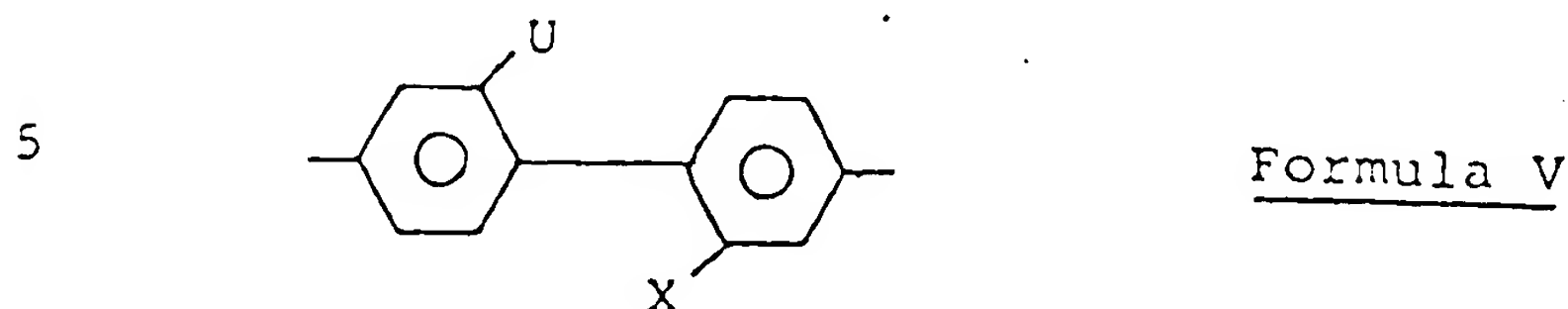
wherein each of U and X is a substituent other than
10 hydrogen. The presence of such non-hydrogen substituents
on each of the aromatic nuclei of the radical promotes a
condition of non-coplanarity. Examples of such preferred
substituents, which may be the same or different, include
halo, nitro, alkoxy and substituted-alkyl (e.g., trifluoro-
15 methyl). While the presence of such non-hydrogen sub-
stituents is preferred from the standpoint of promoting
non-coplanarity, it will be appreciated, from the nature of
substituents W and X set forth in connection with Formula III
hereinbefore, that each X and W can be hydrogen and that,
20 accordingly, substituent U will in such instance desirably
comprise a bulky substituent such as will provide steric
hindrance to a condition of coplanarity.

In the polyamides of the present invention which comprise
25 recurring units represented by the following formula

$$\left[\begin{matrix} O \\ \| \\ C \end{matrix} - A - \begin{matrix} O \\ \| \\ C \end{matrix} - \begin{matrix} R \\ | \\ N \end{matrix} - B - \begin{matrix} R^1 \\ | \\ N \end{matrix}\right]$$ Formula II

$$\begin{matrix} Y \\ | t \end{matrix} \quad z \quad z \quad \begin{matrix} Y \\ | t \end{matrix}$$

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1 In such stilbene radicals, the nature of each Y and Z will
be such as to provide the radical with a non-coplanar
molecular configuration. Preferably, non-coplanarity will
be provided by the presence of a single non-hydrogen sub-
stituent Z. Where each Z is hydrogen, non-coplanarity can
5 be provided by the positioning of a non-hydrogen Y sub-
stituent on at least one aromatic nucleus of the radical in

an ortho relationship to the $-\overset{\overset{Z}{|}}{C}=$ moiety of the radical.
Suitable non-hydrogen Y and Z substituents include, for
10 example, any of those set forth in connection with radicals
U, W and X defined hereinbefore.

Examples of preferred stilbene-type radicals included
within the class represented by Formula IV include the
15 following:
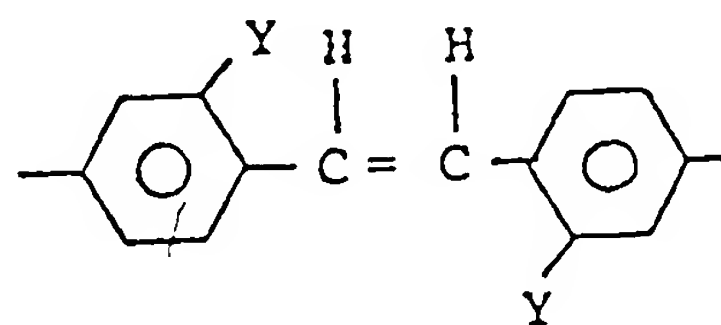
Formula VI

20

where at least one of the Y substituents is other than
hydrogen, preferably, halo or alkoxy; and

Formula VII

25
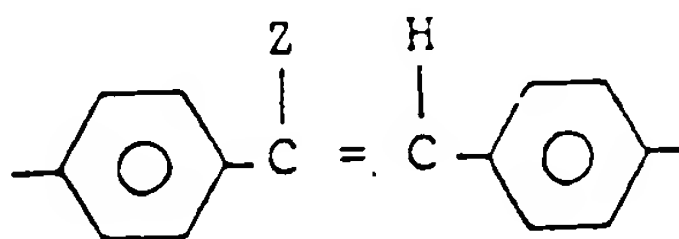
.... other than hydrogen, preferably

Inclusive of polyamides of the present invention represented
by the structure of Formula II are those having recurring
.... represented by the following structures wherein,
unless otherwise specified ....
35 the meanings set forth hereinbefore:

1

$$\left[\overset{O}{\underset{}{\underset{\|}{C}}} - \overset{U}{\bigcirc} - \bigcirc - \overset{O}{\underset{\|}{C}} - \overset{H}{\underset{\|}{N}} - \overset{U}{\bigcirc} - \bigcirc - \overset{H}{\underset{\|}{N}} \right] ; \qquad \underline{\text{Formula VIII}}$$

W_p X_r W_p X_r

5

10

$$\left[\overset{O}{\underset{\|}{C}} - \overset{U}{\bigcirc} - \bigcirc - \overset{O}{\underset{\|}{C}} - \overset{H}{\underset{\|}{N}} - \overset{H}{\underset{\|}{N}} \right] ; \qquad \underline{\text{Formula IX}}$$

W_p X_r

15

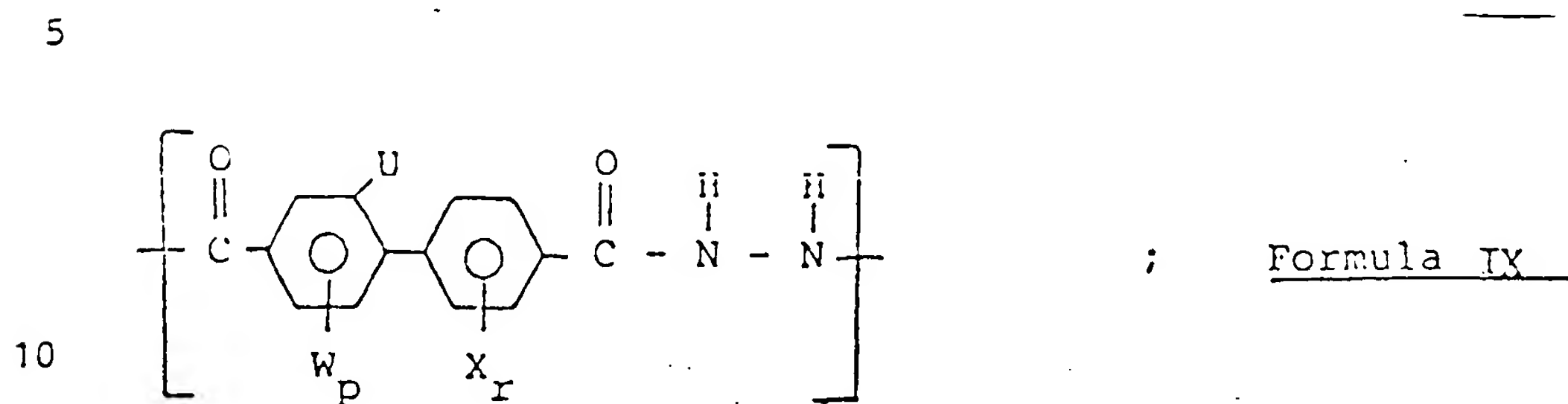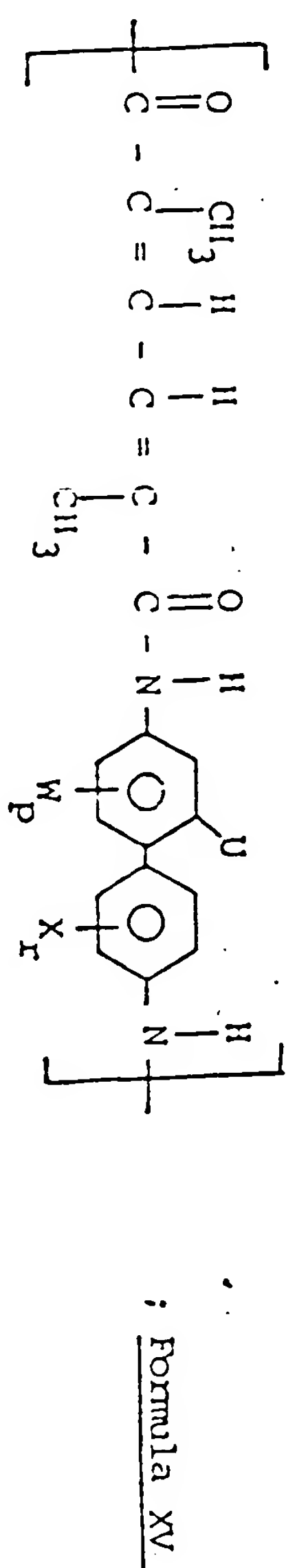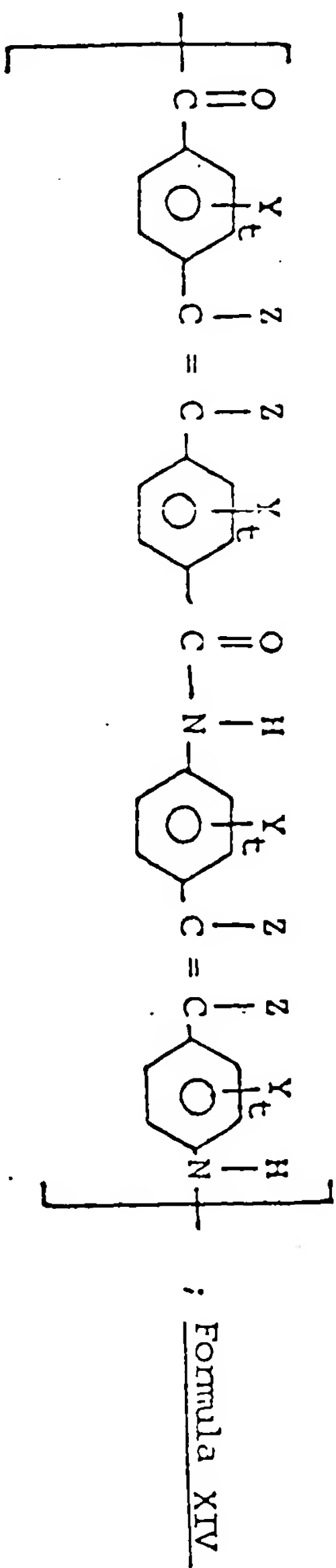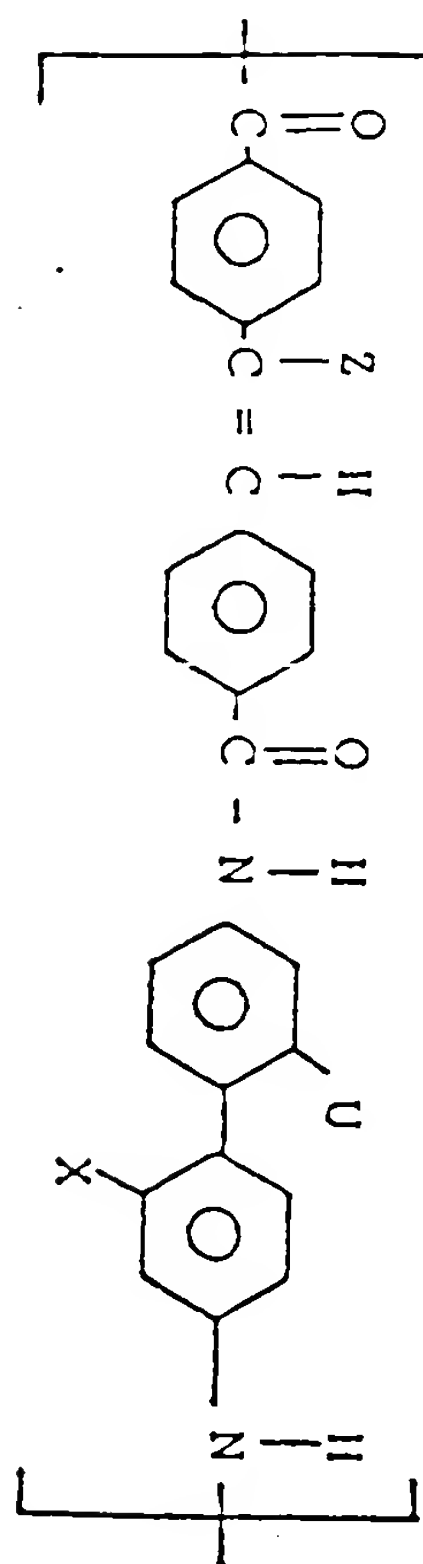$$\left[\overset{O}{\underset{\|}{C}} - \bigcirc - \bigcirc - \overset{O}{\underset{\|}{C}} - \overset{H}{\underset{\|}{N}} - \overset{U}{\bigcirc} - \bigcirc - \overset{H}{\underset{\|}{N}} \right] ; \qquad \underline{\text{Formula X}}$$

W_p X_r

20

$$\left[\overset{O}{\underset{\|}{C}} - \bigcirc - \overset{H}{\underset{\|}{C}} = \overset{}{C} - \bigcirc - \overset{O}{\underset{\|}{C}} - \overset{H}{\underset{\|}{N}} - \overset{U}{\bigcirc} - \bigcirc - \overset{H}{\underset{\|}{N}} \right] ; \quad \underline{\text{Formula XI}}$$

H W_p X_r

25

$$\left[\overset{O}{\underset{\|}{C}} - \overset{U}{\bigcirc} - \bigcirc - \overset{O}{\underset{\|}{C}} - \overset{H}{\underset{\|}{N}} - \overset{Y_t}{\bigcirc} - \overset{Z}{C} = \overset{Z}{C} - \overset{Y_t}{\bigcirc} - \overset{H}{\underset{\|}{N}} \right] ; \quad \underline{\text{Formula XII}}$$

W_p X_r

1

5

10

15

20

25
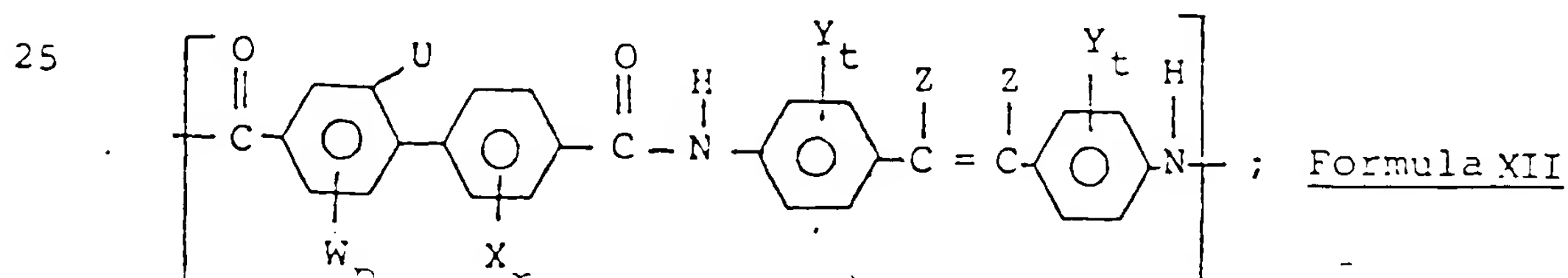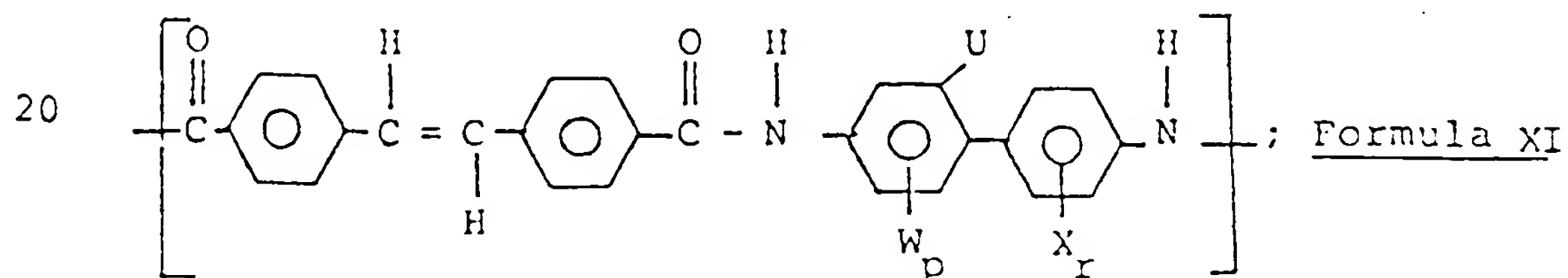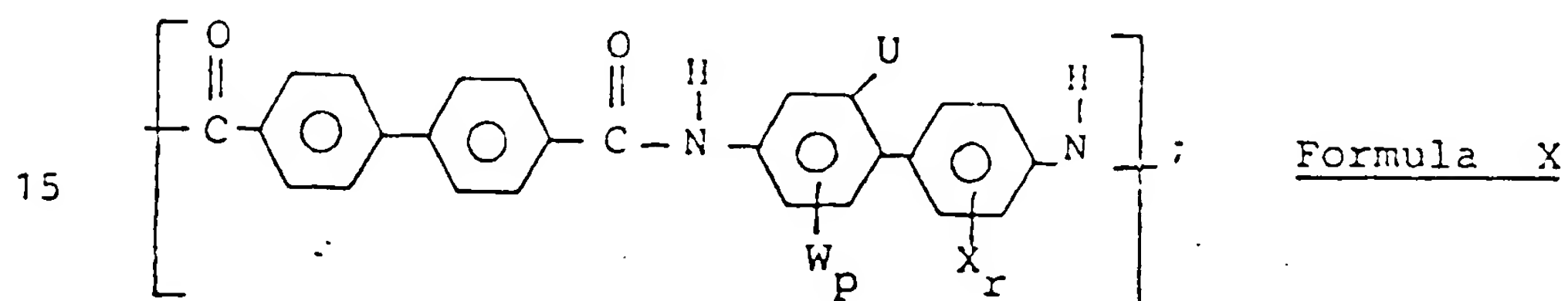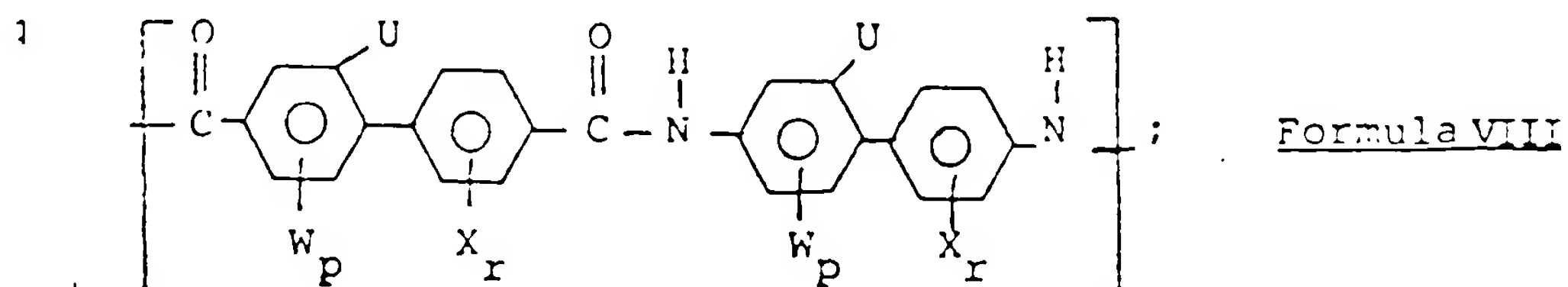
Formula XV ;
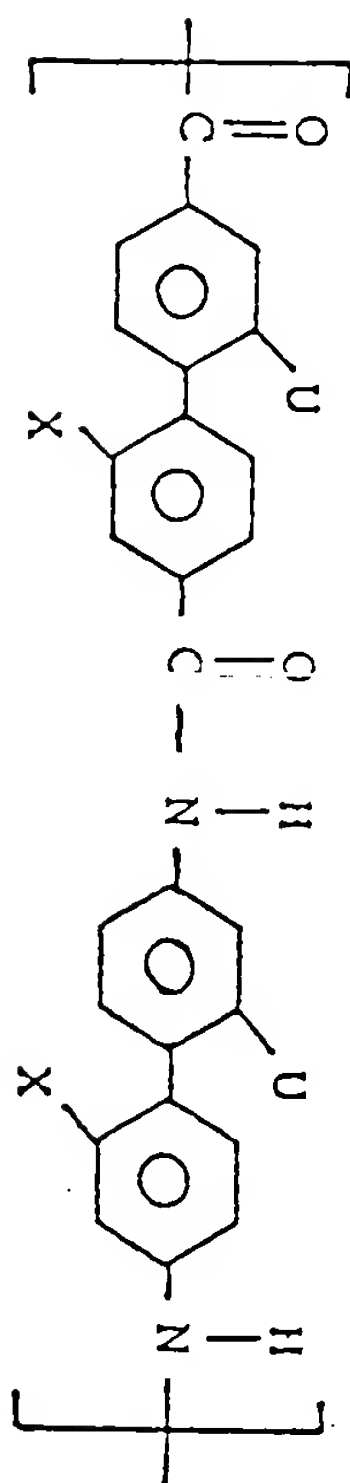
Formula XIV ;

Formula XIII ;

where z and x are other than hydrogen; and

where each x is other than hydrogen.

Formula XVII

Formula XVI

From inspection of the general formula set forth as
descriptive of recurring units of the polyamides, i.e.
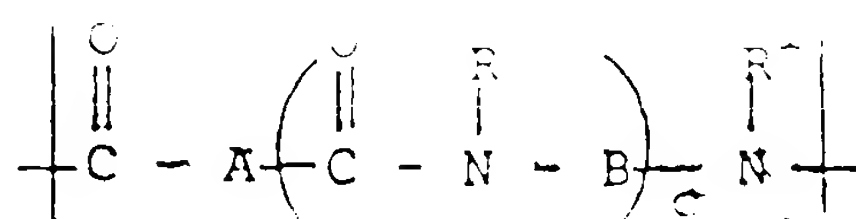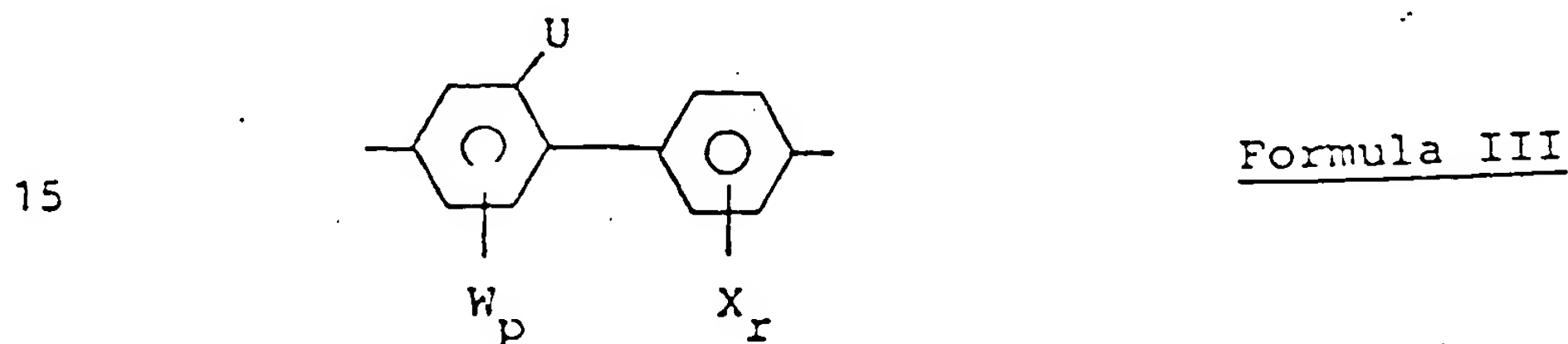
Formula I

1 it will be appreciated that, when c is zero, the recurring
units will be represented by the following formula:

5

$$\left[\begin{matrix} O \\ \| \\ C \end{matrix} - A - \begin{matrix} R^1 \\ | \\ N \end{matrix} \right]$$

Formula XVIII

In such recurring units, radical A will comprise a divalent
radical having a non-coplanar molecular configuration and
10 conforming to the structures of Formulas III and IV set
forth hereinbefore, i.e.,

15

Formula III

or

20
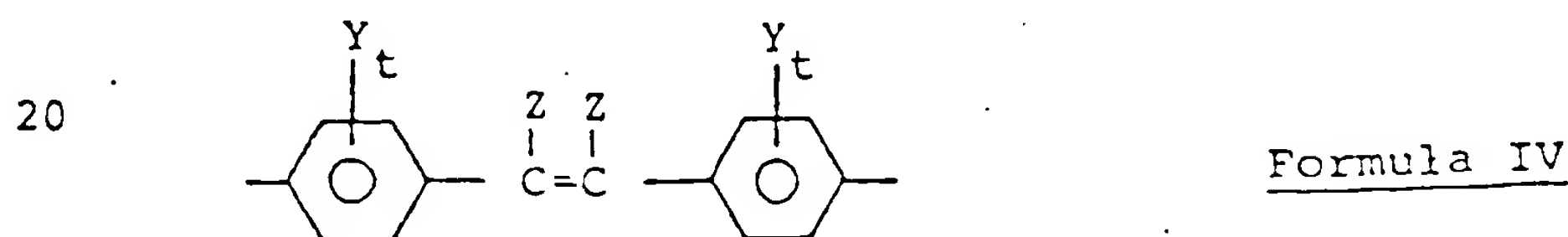
Formula IV

where U, W, p, X, r, Y, t and Z have the same meanings.
25

Inclusive of polyamides represented by the structure of
Formula XVIII are those having recurring units represented
by the following structures wherein U, W, p, X, r, Y

35

1

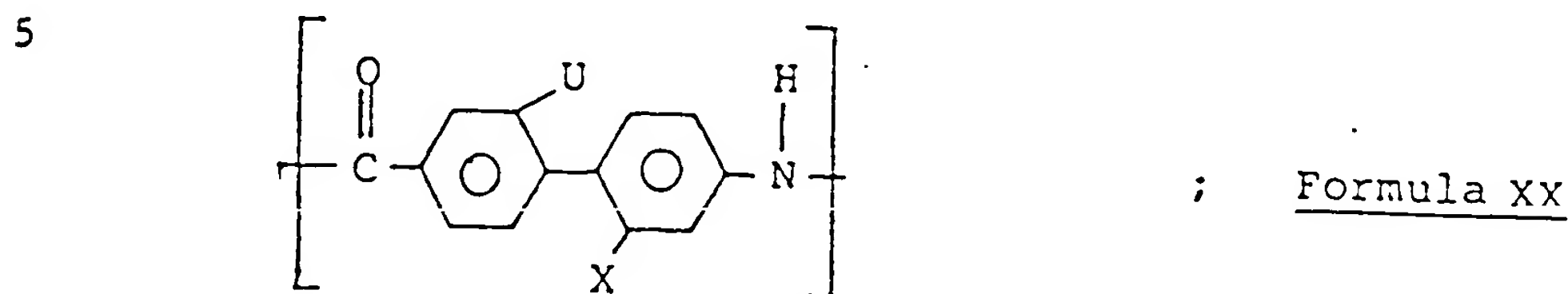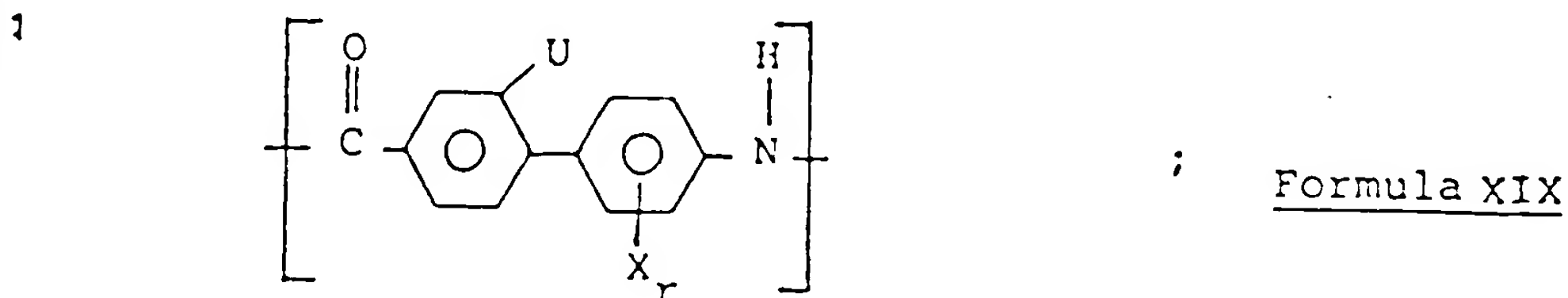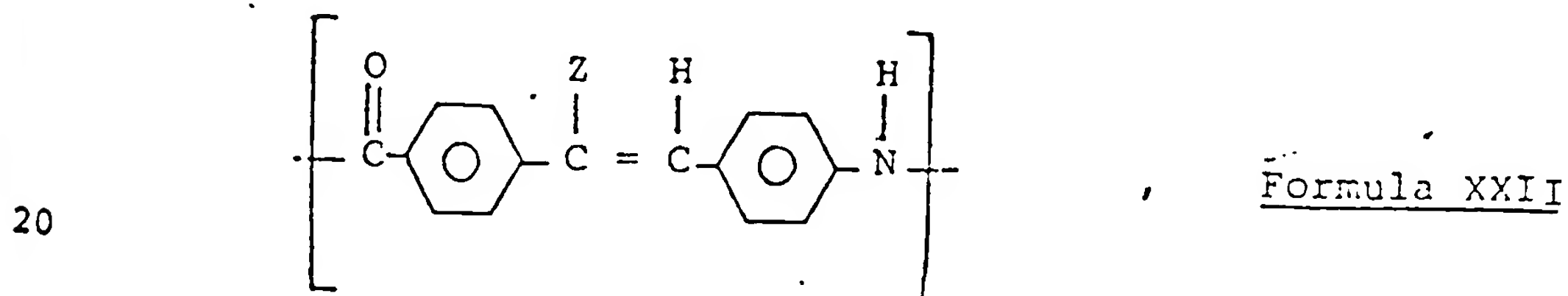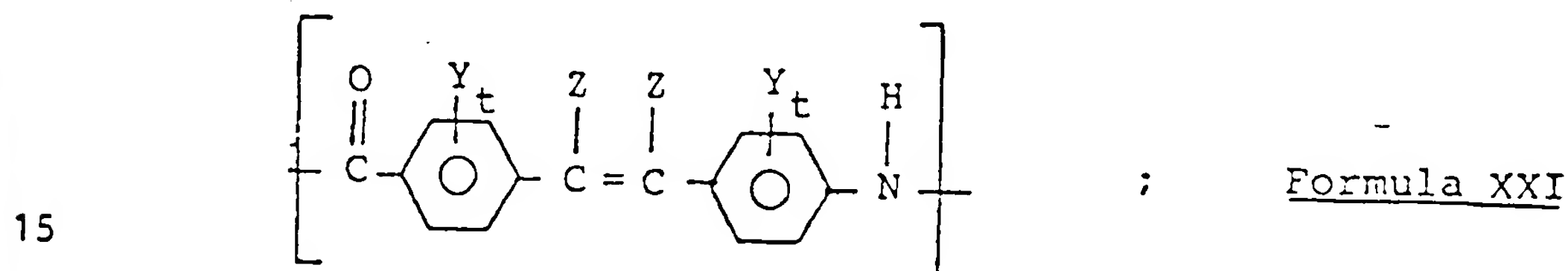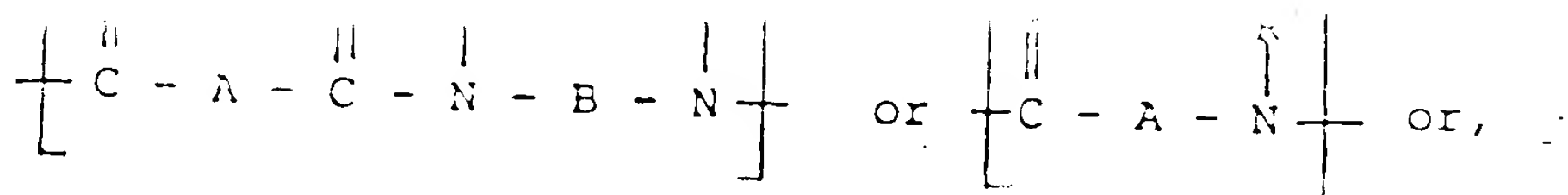$$\left[\begin{array}{c} O \\ \| \\ C \end{array} - \bigcirc\overset{U}{} - \bigcirc\underset{X_r}{} - \overset{H}{\underset{N}{|}} \right] \quad ; \quad \underline{\text{Formula XIX}}$$

5

$$\left[\begin{array}{c} O \\ \| \\ C \end{array} - \bigcirc\overset{U}{} - \bigcirc\underset{X}{} - \overset{H}{\underset{N}{|}} \right] \quad ; \quad \underline{\text{Formula XX}}$$

10 where X is other than hydrogen;

$$\left[\begin{array}{c} O \\ \| \\ C \end{array} - \bigcirc\overset{Y_t}{} - \overset{Z}{\underset{C}{|}} = \overset{Z}{\underset{C}{|}} - \bigcirc\overset{Y_t}{} - \overset{H}{\underset{N}{|}} \right] \quad ; \quad \underline{\text{Formula XXI}}$$

15

$$\left[\begin{array}{c} O \\ \| \\ C \end{array} - \bigcirc - \overset{Z}{\underset{C}{|}} = \overset{H}{\underset{C}{|}} - \bigcirc - \overset{H}{\underset{N}{|}} \right] \quad , \quad \underline{\text{Formula XXII}}$$

20

where Z is other than hydrogen.

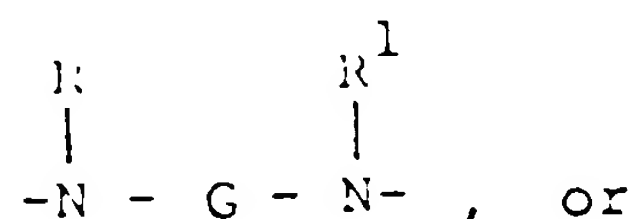25 While the polyamides described herein consist essentially
of recurring units represented by the structures of
Formulas II and XVIII, i.e., recurring units of the
formulas

$$\left[\begin{array}{c} O \\ \| \\ C \end{array} - A - \overset{O}{\overset{\|}{C}} - \overset{|}{N} - B - \overset{|}{N} \right] \quad \text{or} \quad \left[\begin{array}{c} O \\ \| \\ C \end{array} - A - \overset{|}{N} \right] \quad \text{or,}$$
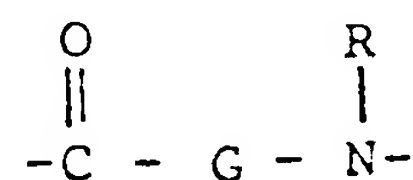
also comprise recurring units not conforming to the described structures of Formulas II and XVIII. Examples of recurring units which do not conform to such descriptions and which can be present in such polyamides in proportions which do not negate the high birefringence of the polymeric material include, for example, recurring units having the formulas
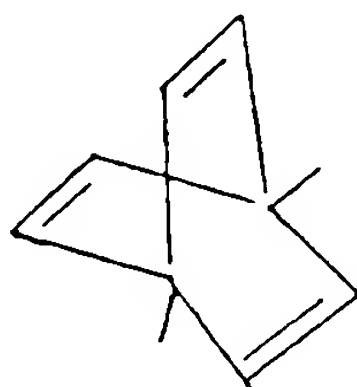
$$-\overset{\overset{\displaystyle O}{\|}}{C} - G - \overset{\overset{\displaystyle O}{\|}}{C} - \quad , \qquad \text{Formula XXIII}$$

$$-\overset{\overset{\displaystyle R}{|}}{N} - G - \overset{\overset{\displaystyle R^1}{|}}{N} - \quad , \quad \text{or} \qquad \text{Formula XXIV}$$

$$-\overset{\overset{\displaystyle O}{\|}}{C} - G - \overset{\overset{\displaystyle R}{|}}{N} - \qquad \text{Formula XXV}$$
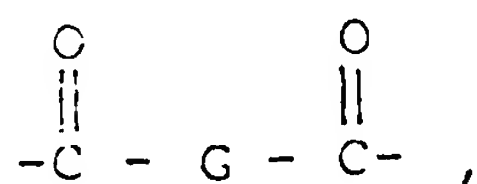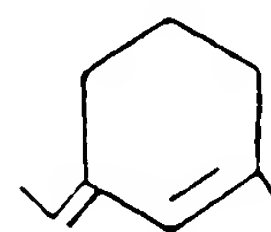
wherein G is a divalent radical such as 1,4-phenylene; 4,4'-biphenylene; vinylene; trans,trans-1,4-butadienylene; 4,4'-stilbene; ethynylene; 1,5-naphthalene; 1,4-dimethyl-trans,trans-1,4-butadienylene; 2,4'-trans-vinylenephenylene; trans,trans-4,4'-bicyclohexylene; 2,5,7-bicyclooctatriene-1,4-,

i.e.,   ; or

other divalent radicals can, however, occur as radicals provided that such radicals do not adversely and materially reduce the birefringence of the polyamide material. It will

saturated moiety where a carbon atom thereof having such unsaturation is to be bonded to an amino group.
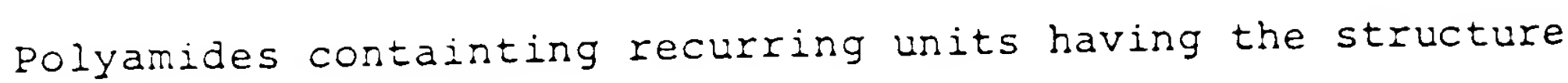
1 The substituted polyamides utilized in devices of the
present invention can be prepared by resort to polyamide
synthesis routes involving the polymerization of suitable
acid halide and amine monomers in an organic solvent which
may contain a solubilizing agent such as lithium chloride

5 or chain-terminating agent where desired. Polyamides of
the type represented by the structure of Formula I can be
prepared, for example, by the reaction of a dicarboxylic acid halide

of the formula $Hal-\overset{O}{\overset{\|}{C}}-A-\overset{O}{\overset{\|}{C}}-Hal$ with a diamine of the formula

10 $H-\overset{R}{\underset{\|}{N}}-B-\overset{R^1}{\underset{\|}{N}}-H$, where Hal represents halogen, such as chloro or
bromo and A and B have the meanings hereinbefore set forth,
except that B cannot represent an aliphatic unsaturated
moiety. The reaction can be conducted in an organic solvent

15 such as N-methyl pyrrolidone (NMP), tetramethylurea (TMU)
or a mixture thereof, and preferably, in the presence of
a salt such as lithium chloride to assist in the solubiliz-
ation of reactant monomers and maintenance of a fluid
reaction mixture. The preparation of a polyamide of the

20 present invention can be illustrated by reference to the
preparation of poly(2,2'-dibromo-4,4'-biphenylene)-trans-
α-bromo-p,p'stilbene dicarboxamide, a preferred polyamide
herein, in accordance with the following reaction scheme:

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$$Cl-C \overset{O}{=} \quad + \quad H_2N \quad NH_2 \quad \xrightarrow[\text{LiCl}]{\text{NMP/THF}}$$

Polyamides containting recurring units having the structure

can be prepared, for example, by the polymerization of a
 . . . . the form of a halide,
 . . . .

1 other salt. This polymerization can be illustrated by reference to the preparation of poly(2,2'-dibromo-4,4'-biphenylene)carboxamide in accordance with the following reaction scheme showing the polymerization of the hydrochloride salt of 2,2'-dibromo-4-amino-4'-chlorocarbonyl-

5 biphenyl:

10
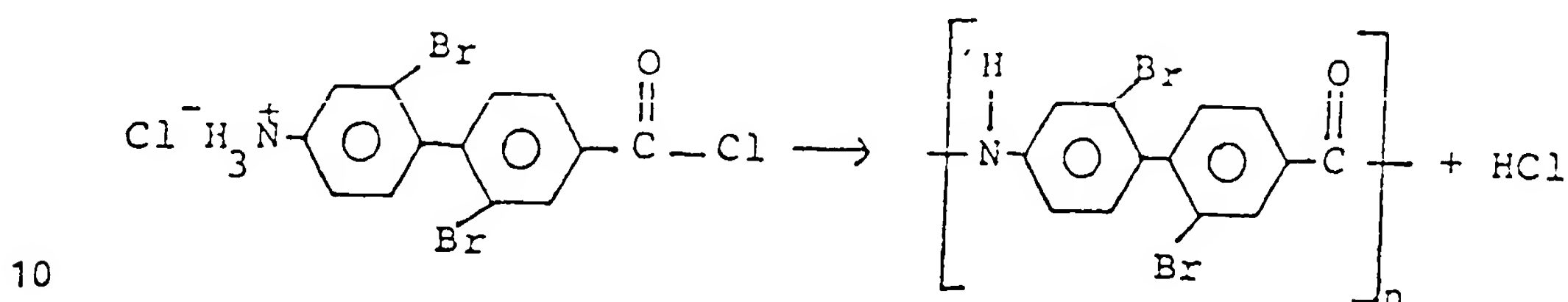
Substituted polyamides useful in optical devices of the present invention can be prepared by polymerization of correspondingly substituted monomers in a suitable organic

15 reaction solvent. Such solvents include amide and urea solvents including N-methyl-pyrrolidone and N,N,N'N'-tetramethylurea. Other suitable reaction solvent materials include N-methyl-piperidone-2; N,N-dimethylpropionamide;

20 N-methylcaprolactam; N,N-dimethylacetamide; hexamethylphosphoramide; and N,N'-dimethylethylene urea. The polymerization can be conducted by dissolving the monomer or monomers to be polymerized in the reaction solvent and allowing the exothermic polymerization reaction to occur

25 usually with the aid of external cooling. In general, the polymerization will be conducted initially at a temperature of from about -20°C to about 15°C, and preferably, in the range of from about -5°C to about 5°C. Thereafter,

melts mass of gel-like consistency. In general, the polymerization reaction will be conducted over a period of from about 1 to 24 hours, preferably about 3 to 18 hours.

While the monomer or monomers to be polymerized can be

1   dissolved in a suitable amide or urea solvent and allowed
to react with formation of the desired polymeric material,
a preferred reaction sequence where a mixture of copoly-
merizable monomers is utilized involves the preparation
of a solution of a first monomer in the amide or urea

5   solvent and the addition thereto of a second or other
monomer or a solution thereof in a suitable organic
solvent therefor, such as tetrahydrofuran. External cooling
of the resulting reaction mixture provides the desired
polyamide material in high molecular weight and minimizes

10   the production of undesired side reactions or by-products.

The polyamide materials prepared as described can be
recovered by combining the polymerization reaction mixture
with a non-solvent for the polymer and separating the poly-

15   mer, as by filtration. This can be effectively accomplished
by blending the polymerization mixture with water and
filtering the solid polyamide material. The polyamide can
be washed with an organic solvent such as acetone or ether
and dried, for example, in a vacuum oven.

20

Polyamide materials as described hereinbefore and methods
for their preparation are described in greater detail in
the European Patent Application of H.G. Rogers, R.A.
Gaudiana, J.S. Manello and R.A. Sahatjian, Attorney

25   Docket No. 3920-X-11.692 filed of even date herewith.

While the transparent highly birefringent materials useful
in the devices of the present invention have been set forth

of other polyamide types, or of types or classes other than
polyamides, can likewise be utilized herein where the

long axis of the polymer.

particularly useful herein are transparent polyamide
materials comprising recurring units corresponding to
Formula I hereof wherein c is zero or one, each of A and
B is a divalent radical, except that B can additionally
represent a single bond, and at least one of A and B is
a substituted-quaterphenylene radical having the formula
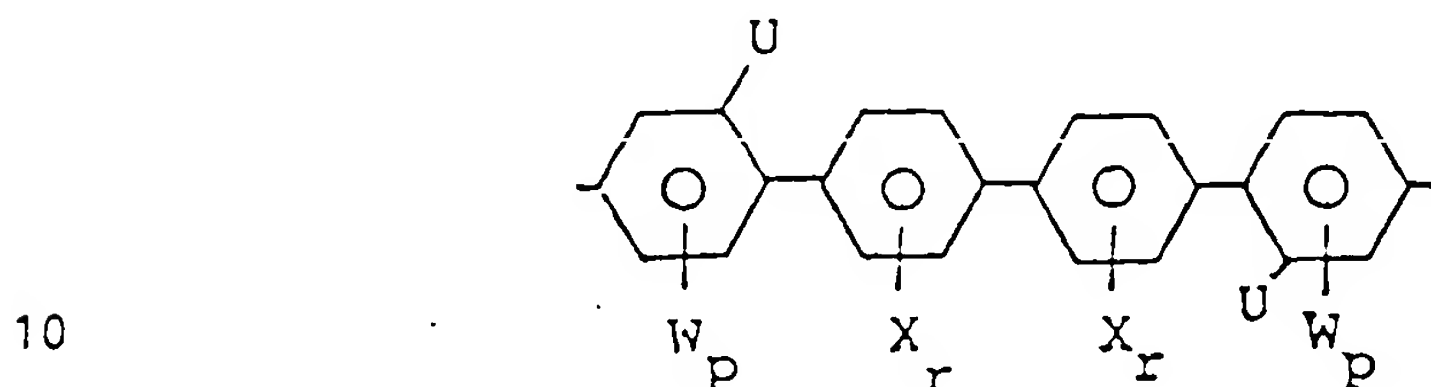
wherein U, W, X, p and r have the meanings set forth
herein and the U, W_p and X_r substitution is sufficient to
provide the radical with a non-coplanar molecular con-
figuration.

The above substituted-quaterphenylene polyamides can be
prepared, for example, by reaction of a suitably sub-
stituted quaterphenylene diamine and a dicarboxylic acid
or halide. These polymers and their preparation are
described in greater detail and are claimed in the
European Patent Application of R.A. Gaudiana and P.S.
Kalyanaraman, (Attorney Docket No. 3920-X-11.692) filed of
even date herewith.

Transparent polymeric materials from classes other than
polyamides and which can be utilized herein include, for
example, polymers having thiazole, imidazole, oxazole

units, where U, W, X, p and r have the meanings herein-
before ascribed, can be utilized herein:

1
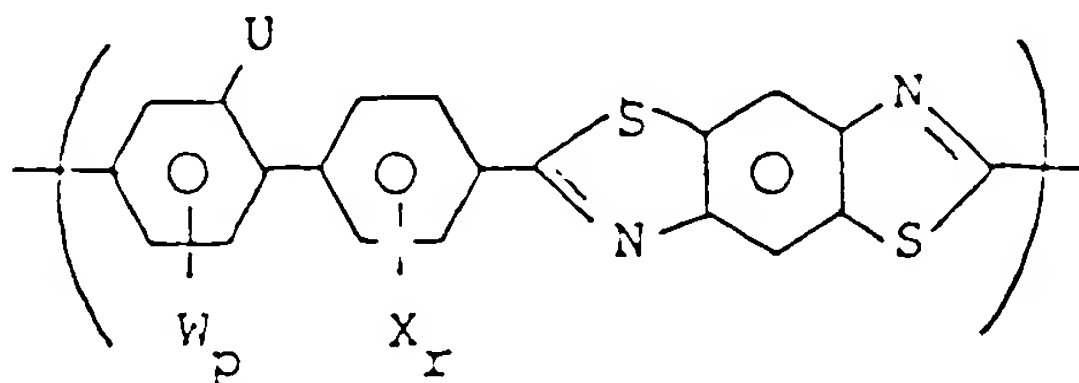
5   Such polymeric materials can be prepared by reaction of a
dicarboxylic acid compound of the formula

10
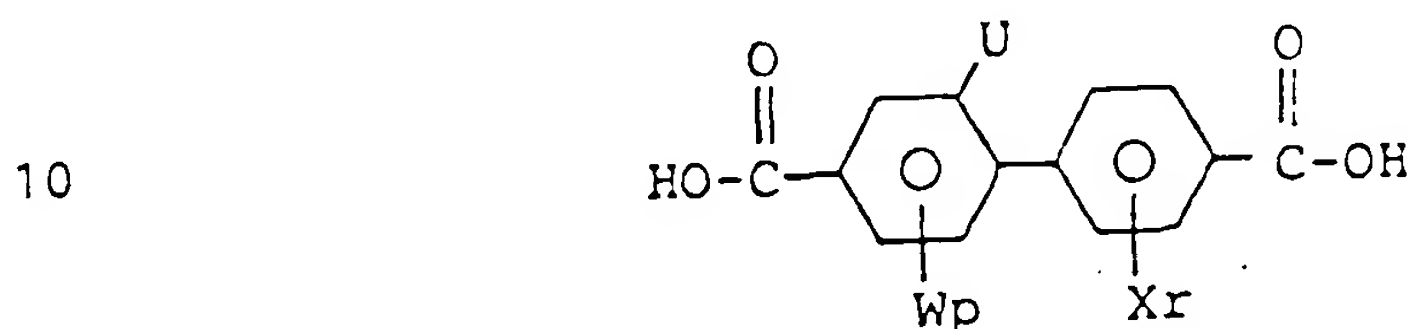
with an amino-thiol of the formula

15
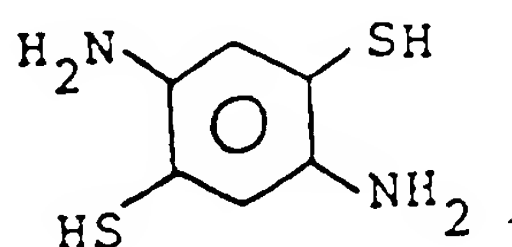
20   in a suitable organic solvent with recovery of the desired
polymeric material.

Polymers comprising the following imidazole-containing
repeating units can also be employed herein, where U, W,
25   X, p and r have the meanings hereinbefore described.

These polymers can be prepared, for example, by reaction

35

1

HO-C(=O)—⟨benzene ring with U, Wp⟩—⟨benzene ring with Xr⟩—C-OH(=O)
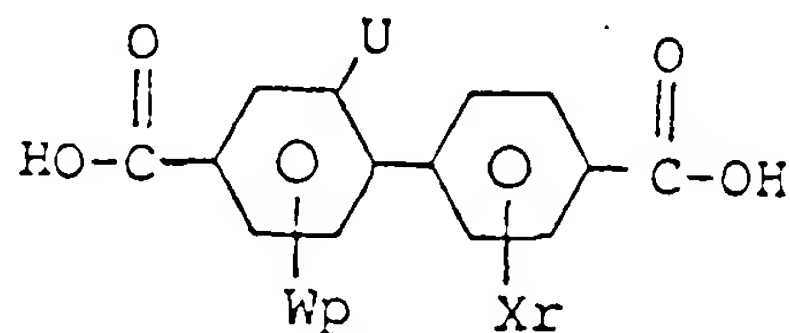
5   with 1,2,4,5-tetramino-benzene.

Polymers containing recurring units having an oxazole
moiety can be suitably prepared by reaction of a dicarb-
oxylic acid compound as aforedescribed with, for example,

10   1,4-dihydroxy-2,5-diamino-benzene, with formation of a
polymer containing the following recurring units where U,
W, X, p and r have the meaning set forth hereinbefore.

15   ⟨polymer recurring unit structure with U, Wp, Xr, oxazole rings with O and N⟩
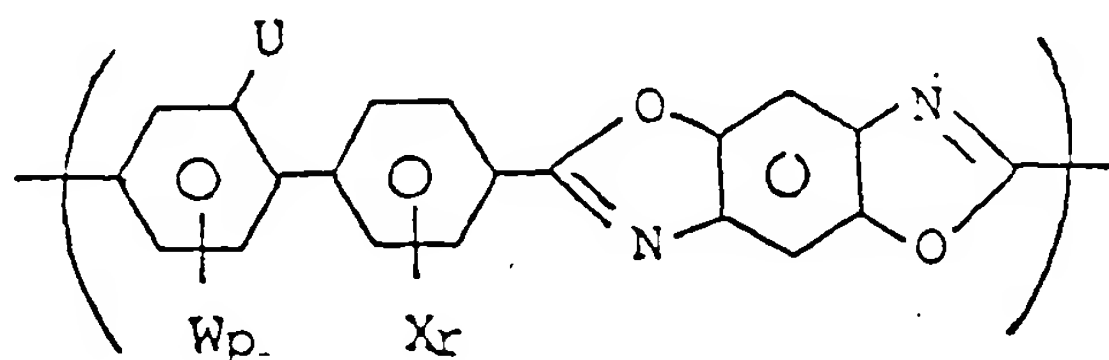
Polyester materials can also be suitably employed herein.
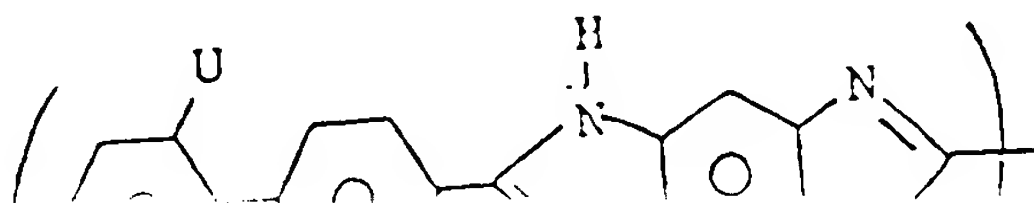20   Exemplary of such polyesters are those having recurring
units of the formula

25   ⟨polymer recurring unit structure with U, Wp, Xr and O-C(=O) linkages⟩
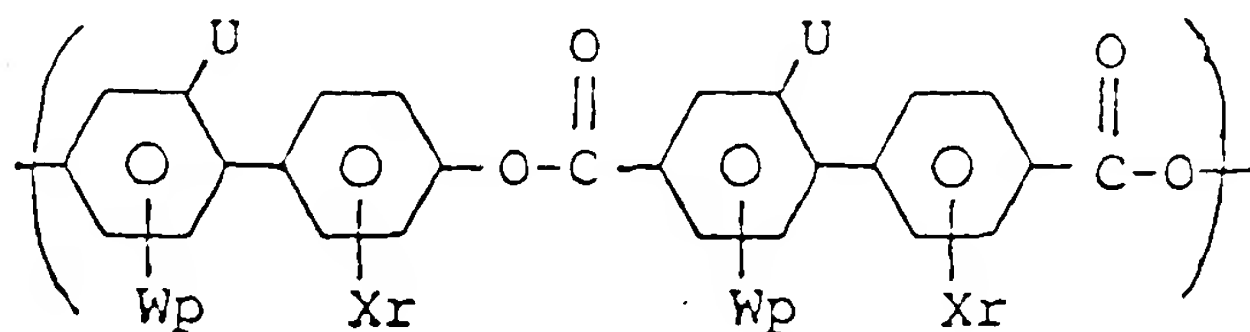
wherein each U, W, X, p and r has the meaning set forth

....
the present invention are polymers comprising recurring
units of the formula

1

$$\left[\begin{array}{c} \overset{O}{\underset{\|}{}} \quad \overset{O}{\underset{\|}{}} \\ -Mu-C-Az-C- \end{array}\right]$$
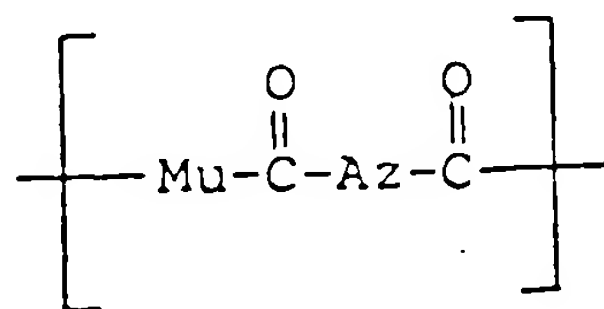
5   where Mu is a divalent radical having the formula

$$\begin{array}{cc} D & E \\ | & | \\ -C=C-C=C- \\ | & | \\ D' & E' \end{array}$$
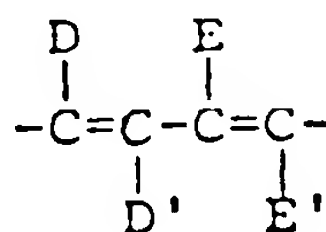
10

where each of D, D', E and E' is hydrogen, alkyl or sub-
stituted-alkyl; and Az is a divalent radical having the
formula

$$\begin{array}{cc} R & R' \\ | & | \\ -N-W-N- \end{array}$$

15

where each of R and R' is hydrogen, alkyl, aryl, alkaryl or
aralkyl and W is a single bond, alkylene or alkenylene; or
Az is a divalent radical having the formula

20

$$-N \begin{array}{c} Y \\ \diagup \quad \diagdown \\ \diagdown \quad \diagup \\ Y' \end{array} N-$$
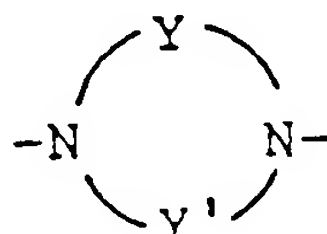
25   where each of Y and Y' represent the atoms necessary to
complete with the nitrogen atoms to which they are bonded
a piperazine or substituted-piperazine radical.

conveniently prepared by reaction of

amine such as piperazine, 2-methylpiperazine or 2,5-di-
methylpiperazine.

the present invention can be variously formed or shaped
into films, sheets, coatings, layers, fibrils, fibres or
the like. For example, a solution of a substituted poly-
amide as described hereinbefore, in a solvent material such
as N,N-dimethyl-acetamide, optionally containing lithium
5   chloride solubilizing agent, can be readily cast onto a
suitable support material for the formation of a polymeric
film or layer of the polyamide material. The polymeric film
can be utilized for the production of a birefringent poly-
meric film or sheet material which can be utilized in an
10   optical device of the invention. Thus, a polymeric film or
sheet material can be subjected to stretching so as to
introduce molecular orientation and provide a film material
having a highly birefringent character.

15   Known shaping or forming methods can be utilized for the
orientation of polymeric materials suited to application
in devices of the present invention. Preferably, this will
be accomplished by unidirectional stretching of a poly-
meric film, by extrusion of the polymer into a sheet,
20   layer or other stretched form, or by the combined effects
of extrusion and stretching. In their oriented state, the
polymers utilized herein exhibit unusually high bire-
fringence. In general, greater birefringence will be ob-
served in the case of polymeric materials exhibiting a
25   greater degree of molecular orientation. It will be
appreciated, however, as has been pointed out hereinbefore,
that the particular molecular structure or configuration of
the polymeric material may affect desired physical

... be realized by stretching or other means. It is a
significant aspect of the present invention, however, that
the polymeric birefringent material which has a high

30   degree of orientation, exhibit unusually high birefringence.

1 In this connection, it is to be noted, for example, that
the substituted polyamides described herein will often ex-
hibit higher birefringence than the more highly oriented
materials of different polymeric structure. For example,
an extruded film of a substituted polyamide hereof
5 comprised of recurring units of the formula
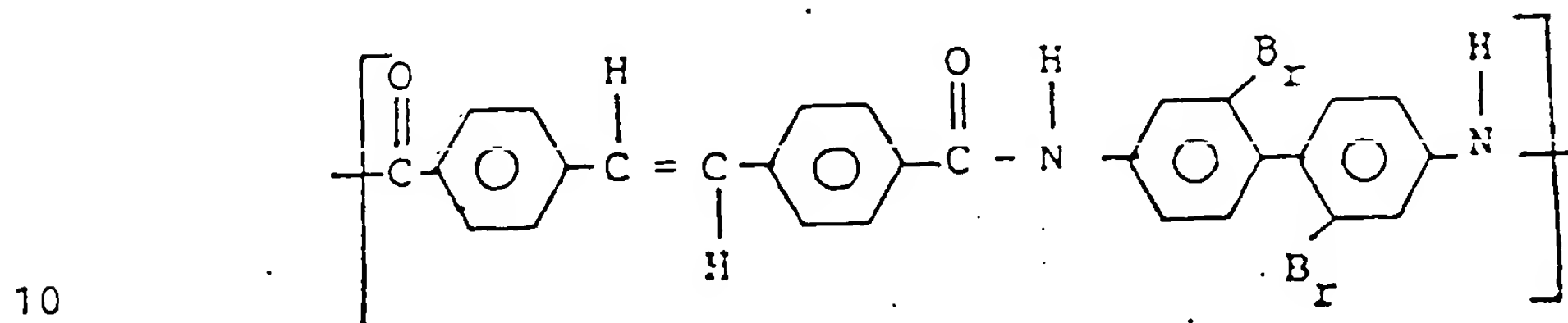
and having a degree of orientation in the range of from
about 80 % to 85 % as determined from infra-red dichroism,
15 exhibited a birefringence (Δn) of 0.865 as measured
utilizing principles of interferometry. In contrast, a
polyamide fibre material and comprised of recurring units
of the formula:
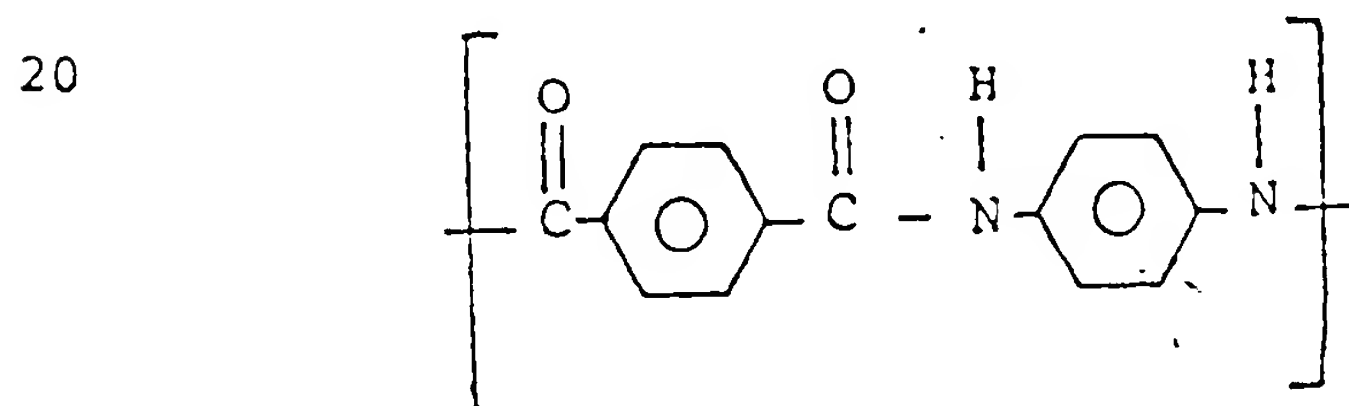
25

is reported in the literature, A.A. Hamza and J. Sikorski,
J. Microscopy, 113, 15 (1978), as having a birefringence
of 0.761, as measured by interferometric technique and at a
degree of orientation of about 90 % to 95 %.

desirably simulate to the maximum practical extent the
optical properties of a uniaxial crystal. Accordingly, the
resultant oriented fibres will exhibit substantially uniaxial
optical properties.

1 Optical efficiency and maximum birefringence will be
realized where such substantially uniaxial behaviour is
exhibited by such polymers.

The molecularly oriented birefringent polymers utilized
5 herein will preferably exhibit a birefringence of at least
about 0.2, and more desirably, a birefringence of at least
0.4. Thus, preferred polymers for use in the articles
hereof will exhibit substantially uniaxial optical behaviour
and a birefringence of at least about 0.2 and will be
10 comprised of recurring units having a geometric index of
about 0.5 or higher.

The birefringent polymeric materials utilized in the
devices of the present invention, in addition to exhibit-
15 ing high birefringent properties, are advantageous from
the standpoint of their transparency. In contrast to poly-
meric materials which become decidedly opaque as a result
of stretching, birefringent materials hereof exhibit
transparency in unoriented and stretched forms. For example,
20 the substituted polyamides described herein exhibit a high
transparency and a low order of light scattering, exhibit-
ing a ratio of amorphous to crystalline material of from
about 10:1 to about 20:1 by weight. These materials are,
thus, suited to optical applications where a light-trans-
25 missive, highly refractive and birefringent material is
desirably utilized. Depending upon the nature of sub-
stituent moieties on the divalent radicals of the re-

are present, a yellow transparent film or fibre can be
fabricated. Films, coated or other shaped forms of the

particular recurring units of the polyamide materials,

1 and particularly the nature of substituent moieties and
   solvent materials, the solubility characteristics of these
   substituted polyamides can be varied or controlled to suit
   particular applications.

5 The birefringent properties of polymers utilized in the
   devices of the present invention can be determined by the
   measurement of physical and optical parameters in accord-
   ance with known principles of physics and optics. Thus,
   for example, the birefringence (Δn) of a suitable bire-
10 fringent polymeric material can be determined by the
   measurement of optical phase retardation (R) and film
   thickness (d) and calculation of birefringence in accord-
   ance with the relationship

$$\Delta n = \frac{R \lambda}{d}$$

15

   where λ represents the wavelength of light utilized for the
   conduct of the measurements. Alternatively, parallel re-
   fractive index and perpendicular refractive index of the
20 film material can be measured utilizing Becke line analysis
   or critical angle measurement.

   A preferred method for determining the birefringence of
   useful polymeric materials involves the measurement of
25 retardation of the polymeric material by a method utilizing
   principles of polarized-light microscopy and interfero-
   metry. Such method provides desired precison and accuracy
   in the measurement of the phase difference between a sample

   light emitted by a low-voltage lamp of a microscope is
   linearly polarized by passage through a polarizer and, in

1   a beam recombinator calcite plate, and through an
analyzer whose transmission direction is vertical to that
of the polarizer (crossed position). In the analyzer the
components vibrating in its absorption direction are ex-
tinguished, whereas the components of both rays in the
5   transmission direction are transmitted and interfere. The
phase difference between sample and reference beams, caused
by the molecular structure or configuration of the poly-
meric sample, is measured with compensators. From these
measurements, the thickness and refractive index of the
10 polymeric material can be determined. By determining index
of refraction of the polymeric sample for both parallel and
perpendicular directions, birefringence can, by difference,
be determined. A suitable method and apparatus for determ-
ining phase retardation, index of refraction and bire-
15 fringence for the polymeric materials utilized herein is
a pol-interference device according to Jamin-Lebedeff
described in greater detail by W.J. Patzelt, "Polarized-
light Microscopy," Ernst Leitz GmbH, Wetzlar, West Germany,
1974, page 92.

20

Preferred optical devices of the present invention are
multilayer devices which include a layer of molecularly
oriented and highly birefringent polymeric material as
described hereinbefore, and in addition, at least one
25 layer of isotropic or birefringent material. The additional
layer or layers whether isotropic or birefringent,
comprises a material having an index of refraction matching

material having an index of refraction matching substant-
ially one index of refraction of the highly birefringent
layer can be suitably bonded to the layer of highly bire-

the molecularly oriented and highly birefringent material
bonded between two layers of isotropic material, the index

1 of refraction of each isotropic layer constituting sub-
stantially a match with an index of refraction of the
molecularly oriented and highly birefringent material.
Such preferred device can be utilized for the polarization
of light and may be termed a "total transmission" light
5 polarizer, i.e., one which is particularly adapted to
polarize a very large portion of incident light. Total
polarizers find application in equipment such as may be
employed for signaling, projection and display purposes,
or the like, and in anti-glare systems for automotive
10 vehicles.

According to another embodiment of the present invention,
a molecularly oriented and highly birefringent material as
defined herein can be suitably bonded to an additional
15 layer of birefringent material. In such an embodiment, one
index of refraction of the molecularly oriented and highly
birefringent material will match substantially one index of
refraction of the additional birefringent material. Similar-
ly, the second index of refraction of the molecularly
20 oriented and highly birefringent material will be sub-
stantially a mismatch with respect to the second index of
refraction of the additional birefringent material. Where
a layer of molecularly oriented and highly birefringent
material is bonded to an additional layer of birefringent
25 material, the direction of orientation of each contiguous
birefringent material will be substantially perpendicular
with respect to the other.

According to another embodiment of the present invention,

light polarizing device, at least one of the layers of
birefringent material comprising a molecularly oriented

1 partly transmits and partly reflects incident light as
separate linearly polarized components vibrating in ortho-
gonal directions.

In Fig. 5 is shown, in considerably exaggerated dimensions,
5 an optical device of the present invention in the form of
light-polarizing sheet material 10 as it would appear in
cross-section, namely, as viewed along a given edge. In
order of arrangement with respect to the direction of a
collimated beam 12 from a light source (not shown) the
10 material is composed of an isotropic, or at least function-
ally isotropic layer 14 having a releatively low refractive
index, a molecularly oriented highly birefringent polymeric
layer 16 and a functionally isotropic layer 18 having a
relatively high refractive index, the layers preferably be-
15 ing laminted or bonded together to form a unitary structure.
It is not essential to the proper functioning of the device
that the layers thereof be bonded together, provided, how-
ever, that adjacent or contiguous layers enclosing an air
layer are maintained paralled to one another. One refract-
20 ive index of the polymeric molecularly oriented and highly
birefringent layer 16 matches substantially that of
layer 14 while the other refractive index thereof matches
substantially the index of refraction of layer 18. For
purposes of illustration, the aforesaid refractive indices
25 may be taken as follows: the refractive index of layer 14
is 1.50; the two indices of layer 16 are 2.00 and 1.50;
and the index of layer 18 is 2.00.

interface between layers 16 and 18 is composed of a
plurality of lens-like or lenticular elements 16b. It will
be noted that the lenticular of the section are the

"lenticular", as employed herein, may broadly be inter-

1 preted as constituting a plurality of surface configurations,
including prismatic elements, as well as those of a strictly
lens-like form. A certain degree of latitude is possible as
to the choice of materials employed in forming the several
layers. Thus, for example, layer 14 may suitably be composed
5 of an isotropic plastic material such as poly(methylmeth-
acrylate) having a refractive index of 1.50. Layer 16 can,
accordingly, be composed of a transparent plastic layer which
for example, has been rendered birefringent as by unidirect-
ional stretching. Suitable for this purpose is the polymeric
10 material, poly[2,2'-bis(trifluoromethyl)-4,4'-biphenylene] 2",
2'"-dimethoxy-4,4'"-biphenyldicarboxamide having refractive
indices of 1.50 and 2.00 when thus rendered birefringent.
Layer 18 can be suitably comprised of or incorporate a trans-
parent isotropic material having an index of refraction
15 approximating the higher index of birefringent layer 16.

One such material is poly(2,2'-dibromo-4,4'-biphenylene)-
4",4"'-stilbenedicarboxamide having an index of refraction
of 2.07. Alternatively, layer 18 can comprise poly(2,2'-di-
20 bromo-4,4'-biphenylene)-α-bromo-4",4"'-stilbenedicarbox-
amide having a refractive index of 2.05.

One method of constructing the sheet material is to form the
birefringent layer 16 by a casting, or a casting and
25 embossing procedure, after its proper solidification, and
casting the isotropic layers 14 and 18 on the opposite
lenticular surfaces thereof. The birefringent layer 16 may
be composed of substantially any material having a bire-

and 18. It may also be formed by any of several different
procedures. Assuming, by way of illustration, that the bi-

1 able material, such as the aforementioned material,
poly[2,2'-bis(trifluoromethyl)-4,4'-biphenylene]-2",2"'-
dimethoxy-4",4"'-biphenyldicarboxamide, i.e. a sheet of a
given length and predetermined thickness, can be first
extruded or cast. The sheet can then be subjected to a
5 mechanical stress in a longitudinal direction to elongate
and molecularly orient it, as by a stretching operation in
the presence of heat or other softening agent, or by a cold
drawing method, or, again, by applying amechanical stress
to its surface. The direction of stretch or other applicat-
10 ion of orienting stress is to be taken as having been per-
formed toward and away from the viewer, namely, in a
direction normal to the plane of the paper. This being the
case, the optic axis 20 of layer 16 constitutes a direction
both in the plane of layer 16 and normal to the plane of the
15 paper.

Birefringent layer 16, having acquired the desired bire-
fringence as, for example, a birefringence of 1.50 and 2.00,
assuming the stated refractive indices, can then be sub-
20 jected to surface modification to form thereon the converg-
ing or positive lenticular elements 16a and the diverging
but functionally converging or positive lenticular ele-
ments 16b. This can be suitably performed by passing the
material between embossing means such as embossing blades,
25 wheels or the like, the surfaces being slightly softened as
by a solvent or heat, or both, as may be necessary during
their treatment but not to such an extent as would relax
the material and alter the previously provided orientation

ingly, the lenticules, as illustrated, are generally
cylindrical with their axes extending parallel to the

1 predetermined separation and focusing of the respective
  rays. While lenticular means of the type described con-
  stitute one preferred configuration, they may be so formed
  as to extend in other directions of the sheet or even have
  a spherical shape, provided that their refractive
5 characteristics are properly chosen and the birefringence
  of the material is suitable. Alternatively, the lenticules
  may be formed by a grinding and polishing procedure or the
  sheet may be stretched or otherwise treated for orienting
  its molecules after the lenticules have been formed thereon.

10
  After completion of the surfacing of the birefringent
  layer 16 and either prior to or after its orientation, the
  isotropic layers 14 and 18 are assembled therewith or formed
  thereon by any appropriate method such as by casting them
15 in liquid form on the preformed layer 16. Assuming that the
  material of layers 14 and 18 is not of a type to cause any
  disturbing double refraction of light rays when solidified
  and subjected to mechanical stress, as by stretching, the
  stretching and desired molecular orientation of layer 16
20 may be accomplished after casting and solidifying layers 14
  and 18 on its surfaces, the entire sheet 10 then being
  stretched as a unit. Or, the layers 14 and 18 may be cast
  on layer 16 after orientation of the latter. Alternatively,
  and again assuming layers 14 and 18 to be substantially
25 incapable of becoming birefringent when stressed, they may
  be preformed so as to have the lenticular surfaces shown,
  superimposed in correctly spaced relation, the bire-
  fringent layer 16 formed therebetween in a fluid state and
  the assembled unit then stretched. In a further

  relation therewith, after the layer 16 has been treated to
  acquire a proper birefringence.

1   lenticules 16a and 16 b are relatively offset from left to
right, that is transversely of the sheet 10, so that the
vertices of lenticules 16a are optically aligned with the
longitudinal edges or intersections of lenticules 16b.
While the lenticules 16a and 16b are shown as being
5   spherical and of similar radii of curvature it will be
understood that neither of these conditions is essential,
per se, the choice depending in general upon the direction
in which the rays are required to be refracted, the extent
of their travel in said directions, and such factors as the
10   refractive indices and thicknesses of the layers.

The collimated beams 12, emanating, for example, from a
light source and reflector of a headlamp (not shown) and
normally incident upon the isotropic layer 14, are trans-
15   mitted without deviation through the latter to the converg-
ing cylindrical lenticules 16a of birefringent layer 16.
At layer 16 each beam is resolved into two components, that
is an ordinary or "O" ray 12a and an extraordinary or "E"
ray 12b. Bearing in mind that the refractive index of
20   isotropic layer 14 has been given as 1.50 and the refractive
indices of birefringent layer 16 as 1.50 and 2.00 let it be
assumed that the 1.50 refractive index applies to the
components 12a which, for purposes of illustration, will be
considered the ordinary rays vibrating substantially at
25   right angles to the optic axis. Inasmuch as these rays have
a refractive index which is essentially identical to that
of layer 14, which precedes layer 16 in order of their
travel, they are refracted by lenticules 16b so to converge

Inasmuch as the refractive index of 1.50 and that of
layer 14 are substantially identical. The components 12b,
which in this instance are taken as the extraordinary ray
optic axis and having a refractive index of 2.00 identical

1 to that of the isotropic layer 18, are refracted by the
lenticules 16a because of the dissimilarity of respective
refractive indices. However, the diverging or negative
lenticular surface 16a constitutes, in effect a converging
lenticular surface of isotropic layer 14, the components 12

5 thereby being refracted convergently toward the aforesaid
theoretical focal plane. As described, the layer 16 is
positively birefringent inasmuch as the refractive index
of the E ray is represented as greater than that of the
O ray, but a reverse condition is possible. The rays 12a

10 and 12b, generated in birefringent layer 16 are plane
polarized, their vibration directions being at 90° to one
another as indicated. The rays are thence transmitted with
alteration of their state of polarization with their vibr-
ational planes normal to one another.

15

Either the E or the O ray, or both, may be selectively
treated, as by passing them through retardation materials,
to provide their vibrations in a single azimuth as will be
described below. Even without such treatment and a non-

20 uniformity of vibration directions, the sheet material of
Fig. 5 has certain uses such, for example, as for
illumination purposes where it is desired to polarize the
light partially in a given direction; for three-dimensional
viewing or for any function wherein transmission of a large

25 part of the incident light is of importance but wherein
completely uniform polarization throughout a given area is
not essential. While the entering rays 12 are shown as
collimated at 90° to the plane of the sheet, a slight
departure from this condition, from left-to-right in the

deviation therefrom may exist in a direction along the
axis of the lenticules.

refraction of rays generally similar to that shown in Fig. 5, the several layers may be formed of substantially any materials having suitable refractive indices, transparency and physical or mechanical properties such as thermal stability, flexibility or adhesion. Thus, for example, layer 14 may be composed of any of such materials as tetrafluoroethylene, vinyl acetate, cellulose acetate butyrate, an acrylic material, glass or the like. Birefringent layer 16 can be, for example, poly[2,2'-bis(trifluoromethyl)-4,4'-biphenylene]-4",4"'-stilbenedicarboxamide having indices of refraction 1.61 and 2.48 or a layer of poly(2,2'-dibromo-4,4'-biphenylene)-4",4"'-stilbenedicarboxamide having indices of 1.77 and 2.64. Layer 18 can be a polymeric material which has been rendered birefringent but which has its optic axis or direction of molecular orientation at 90° to that of layer 16, it being understood that its lenticular surface would match with that of layer 16 at 16b.

In an optical device of the present invention, the indices of refraction of the several layers can be modified or adjusted in predetermined manner such that the proper functional relation beween the indices of refraction of the several layers is maintained. Thus, the indices of refraction of the several layers may be controlled in predetermined fashion by altering plasticizer content. For example, the index may be lowered by the addition of plasticizer. Where bonding substances or subcoats are employed in laminating preformed layers, a material used for such a purpose should

According to another embodiment of the present invention there is provided a light-polarizing element comprising a

1   Such an element can be utilized in a device such as the
    headlamp of an automotive vehicle.

    In Fig. 6 there is shown a headlamp 30 which includes a
    specularly reflecting parabolic mirror 32, a filament 34,
5   a diffusely reflecting plate element 36 and a light-polar-
    izing sheet material 40. Light-polarizing element 40 in-
    cludes a prismatic layer 42 of molecularly oriented and
    highly birefringent polymer and an isotropic layer 44, the
    refractive index of the isotropic layer 44 substantially
10 matching the low index of refraction of birefringent
    layer 42. Thus, for example, birefringent layer 42 may have
    refractive indices of 2.00 and 1.50 and layer 44 a refract-
    ive index of 1.50. An unpolarized collimated beam 12, upon
    entering birefringent layer 42, is resolved into O and E
15 components 12a and 12b, as previously described in connect-
    ion with the device shown in Fig. 5. The prism elements
    of birefringent layer 42 are so formed and disposed relative
    to the incident collimated beam 12 that the E ray 12b is
    reflected rearwardly to the parabolic mirror 32, is
20 reflected to diffusely reflecting element 36, whereat it
    is depolarized, is reflected to mirror 32 and thence to
    light-polarizing sheet material 40 as a second collimated
    unpolarized beam 12d. The prism elements, may for this
    purpose, appropriately be prisms or so-called hollow corner
25 cubes which have the characteristic of reflecting collim-
    ated light rays in the direction whence they came. The
    O ray 12a is transmitted without deviation straight through
    layer 44 which matches its refractive index. This procedure
    repeats itself ad infinitum, it being apparent that

    form azimuth of polarization.

    In accordance with one embodiment of the present in-

1   device effective to linearly polarize a large portion of
the light incident thereon and to transmit substantially
all of one polarized component of light while reflecting
substantially all of the orthogonally polarized component.
Such a polarizer is shown in Fig. 7 as polarizer 50 having
5   alternate layers 54 and 56 of molecularly-oriented, highly-
birefringent material and of isotropic or functionally iso-
tropic material.

The layers 54 are each composed of a molecularly oriented
10   birefringent material. For instance, the material may
comprise poly[2,2'-bis(trifluoromethyl)-4,4'-biphenylene] 2",
2"'-dimethoxy-4",4"'-biphenyldicarboxamide. Other materials
can also be utilized in forming the birefringent layer and
should be selected to have as great a difference between the
15   two indices of refraction as possible since the number of
layers in the polarizer can be substantially decreased when
using birefringent materials having a greater difference
between their indices of refraction.

20   The isotropic layers 56 may be composed of a number of
different materials with the requirement that its refract-
ive index substantially match one of the refractive indices
of the birefringent material layers on either side thereof.
Some examples of materials which are useful for this
25   purpose include polyacrylates, poly(2,2'-dibromo-4,4'-bi-
phenylene)4",4"'-stilbenedicarboxamide, silicon oxides or
titanium dioxides. The isotropic layers can be provided,

layers interleaved therebetween.

1   use of a stretch orientation operation. Layer thickness can be suitably controlled by the extrusion process and allowances for dimensional changes expected in the layer thickness during the stretching step can be made.

5   Fig. 7 schematically shows a number of light rays 62 incident on polarizer 50 and traveling in a direction perpendicular to the surface thereof. As an example, the birefringent layers 54 may have a pair of refractive indices of n_O = 1.50 and n_E = 2.00 and the refractive index of each

10   isotropic layer may be taken as n = 1.50. As each ray 62 passes through the first birefringent layer 54, it is resolved thereby into two components shown as separate rays, namely, an extraordinary or "E" ray 62a for which the birefringent layer has the higher index n_E = 2.00 and an

15   ordinary ray or "O" ray 62b for which the birefringent layer has, for example, the lower index n_O = 1.50, the rays traveling in a similar direction and with their vibration azimuths relatively orthogonally disposed as depicted in the drawing. As shown in Fig. 7, a portion 62c of the "E"

20   rays 62a is reflected at the first interface 64 reached, it being recalled that the refractive index of an isotropic layer was given at n = 1.50. The reflection is due to the refractive index discontinuity at the interface between the layers 54 and 56 which exists for the "E" polarization but

25   not the "O" polarization. For purposes of illustration the reflected light rays 62c are shown as being reflected at a slight angle while in actuality they are reflected straight back in the direction of rays 62a. Thereafter each interface will reflect a further portion of ray 62a

that of layer 56 and in fact, these rays 62b will pass through all layers 54 and 56 unreflected and comprise that

transmitted thereby.

In order to greatly increase the reflectivity of the
polarizer 50 each layer 54 and 56 is made to have an
optical thickness of one-quarter the length of a selected
wavelength. The optical thickness is equal to the physical
thickness multiplied by the index of refraction of the
layer material. The wavelength selected is preferably in
the middle of the visible spectrum, for example, 550 nm so
that the polarizer is effective over a substantial range of
visible light. This arrangement utilizes optical inter-
ference to enhance the efficiency of the polarizer. The
following discussion relates to phase changes in a light
wave, not to changes in the polarization azimuth of the
light wave. In alalyzing the optical properties of the
polarizer, it is important to remember that light suffers a
phase change of π on reflection when it goes from a medium
of low refractive index to a medium of higher refractive
index while it suffers no phase change on reflection when
it goes from a medium of high refractive index to a medium
with a lower refractive index. Thus, in Fig. 7, a light
ray such as 62a, as it passes through the first quarter-
wave birefringent layer 54 will suffer a phase change $\pi/2$.
As the light ray strikes the first interface 64 part of it
is reflected back through the first birefringent layer 54
again suffering a phase change of $\pi/2$, the total phase
change being equal of $\pi/2 + \pi/2 = \pi$. Note that the ray 62a
suffers no phase change on reflection at interface 64 due
to the rule as stated above. Now as the remaining portion of
ray 62a strikes the second interface 66, it has traveled
through two layers suffering a phase change of $\pi/2 + \pi/2$

$+ \pi/2 + \pi$ or 3π. Thus, in accordance with this analysis,
the ray 62a will always suffer a phase change of some
π

component 62c of ray 62a and other such similar rays will reinforce one another resulting in substantially total reflection of the one polarized component of incident light represented by ray 62a providing the number of layers and interfaces are sufficient. The other component 62b will pass undisturbed through the multilayer polarizer 50 so long as the refractive index of the isotropic layers 56 match one of the refractive indices of the birefringent layers 54. Since substantially none of the rays 62a are transmitted, the entire amount of light output from polarizer 50 consists of rays 62b, all polarized in one direction.

In Fig. 8 is shown an optical beam-splitter device of the present invention embodying a layer of birefringent poly-mer. Beam splitter 70 comprises prisms 72a and 72b of iso-tropic material such as glass joined in a Nicol configurat-ion with a layer 74 of molecularly oriented birefringent polymer therebetween. Elements 72a and 72b can be composed of a variety of glass or other isotropic materials and will have a perpendicular index of refraction greater than that of the polymer layer 74 between such elements. For example, a unidirectionally stretched layer 74 of poly-[2,2'-bis(trifluoromethyl)-4,4'-biphenylene]-2,2'-dimethoxy-4,4'-biphenyl having a perpendicular index of refraction of about 1.65 and a unidirectional stretch direction as indicated in Fig. 8 can be utilized between isotropic glass elements 72a and 72b of refractive index 1.8. In operation, unpolarized light 76 enters element 72a and a portion
~~is reflected~~ at the interface of element 72a and

from element 72b as oppositely plane-polarized.
Light 76 is thus split into separate beams of oppositely

1   While particular embodiments of the present invention
utilizing polymeric birefringent layers have been described
in connection with the devices shown in Figs. 5 to 7,
other devices utilizing such polymeric birefringent layers
can also be prepared. Examples of other devices which can
5   be adapted to inculde a polymeric and highly birefringent
layer as described herein are described, for example, in
U.S. Patent 3,506,333 (issued April 14, 1970 to E.H. Land);
in U.S. Patent 3,213,753 (issued October 26, 1965 to H.G.
Rogers); in U.S. Patent 3,610,729 (issued October 5, 1971
10   to H.G. Rogers); in U.S. Patent 3,473,013 (issued
October 14, 1969 to H.G. Rogers); in U.S. Patent 3,522,984
(issued August 4, 1970 to H.G. Rogers); in U.S. Patent
3,522,985 (issued August 4, 1970 to H.G. Rogers); in U.S.
Patent 3,528,723 (issued September 15, 1970 to H.G. Rogers);
15   and in U.S. Patent 3,582,424 (issued June 1, 1971 to K.
Norvaisa). Still other devices that can be prepared
utilizing a birefringent polymer hereof include Wollaston
prisms, Rochan prisms, Fuessner prisms, Brewster polarizers,
non-polarizing beam splitters, compensators and the like.
20
The following non-limiting examples are illustrative of
the present invention.

Example 1

25
This example illustrates the preparation of poly(2,2'-di-
bromo-4,4'-biphenylene)-p,p'-biphenylene dicarboxamide and
the preparation therefrom of birefringent polymeric films.

chloride drying tube) was heated while simultaneously
flushing the vessel with nitrogen. After the reaction

2,2'-dibromobenzidine were added while maintaining a positive nitrogen pressure. The reaction vessel was fitted with a thermometer and a rubber stopple (a rubber membrane-like sealing lid capable of receiving a syringe and of sealing itself upon removal of the syringe). 10 ml of anhydrous distilled N-methylpyrrolidone (NMP) and 15 ml of anhydrous distilled tetramethylurea (TMU) were carefully added with the aid of syringes. The resulting mixture was stirred and warmed to 40°C until all solids had dissolved. The solution was then cooled in a bath of ice and salt to a temperature of -5°C. A small amount of lithium chloride precipitation was observed. Recrystallized p,p'-biphenylene dicarbonyl chloride (0.4689 g; 0.001679 mole) was quickly added by means of a funnel to the stirred 2,2'-dibromo-benzidine solution. An additional 5 ml of TMU were added through the funnel to the reaction mixture. The temperature of the reaction mixture did not rise above a temperature of 7°C. After stirring for 60 minutes, the reaction mixture began to thicken and streaming brefringence (but not stir opalescence) was observed.

The ice bath was removed from the reaction vessel and the temperature was observed to rise to 20°C in 30 minutes at which point the reaction solution became milky in appear-ance. The reaction vessel was placed in an oil bath (40°C) and the reaction mixture was warmed for 30 minutes. The reaction mixture became clear. The temperature of the reaction mixture rose during the warming to a maximum temperature of 55°C at which temperature the reaction mixture was stirred for 1 hour. The reaction product, a

200 ml of ice-water in a blender. The resulting solid was filtered and washed (in the blender) twice each the product was dried in a

product, obtained in 95.4 % yield, was a white fibrous polymeric material having the following recurring structural units:
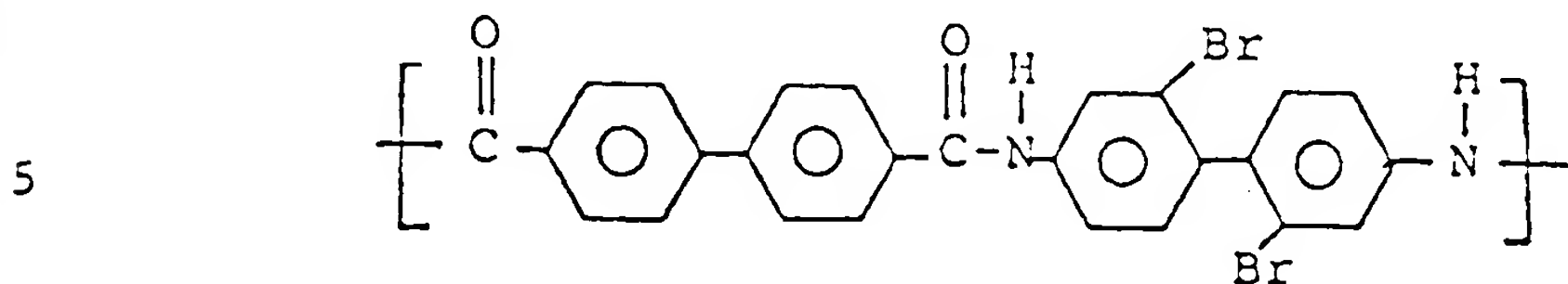
The inherent viscosity of a polymer solution (0.5 g of the polymer of Example 1 per 100 ml of a solution of 5 g lithium chloride per 100 ml of dimethylacetamide) was 3.54 dl/g at 30°C.

Molecular structure was confirmed by infrared spectroscopy. Inspection of the ultraviolet/visible absorption spectrum for the polymer of Example 1 (in 5 % wt./vol. lithium chloride/dimethylacetamide) showed a λ_{max} of 320 (ε = 75,000).

Elemental analysis for $C_{26}H_{16}Br_2N_2O_2$ provided the following:

	%C	%H	%Br	%N	%O
Calculated:	56.97	2.92	29.16	5.11	5.84
Found:	56.86	3.25	28.72	5.10	6.07 (by difference)

Polymeric films were prepared from the polymeric material of Example 1 by casting (onto glass plates) solutions of the polymeric material in a 5 % wt./vol. solution of lithium chloride and dimethylacetamide (5 g lithium chloride per

solution. In each instance, the glass plate carrying the puddle-cast polymer solution was immersed in water (after

1 film separated from the glass plate. The resulting film
was soaked for several hours in water to effect extraction
of occluded lithium chloride and solvent, soaked in acetone
and dried in a vacuum oven at 90°C and 15 mm pressure.
Refractive index, measured by interferometry, was 1.93.

5

Stretched polymeric films were prepared in the following
manner. Water-swollen films (obtained by soaking the poly-
mer films for several hours for removal of occluded lithium
chloride and solvent as aforedescribed) were cut into
10 strips. The strips were mounted between the jaws of a
mechanical unidirectional stretcher. The strips were
stretched (in air at 220°C) to about 50 % elongation, to
effect film orientation. The resulting films were optically
transparent. Birefringence, measured with the aid of a
15 quartz wedge, was 0.293.

Example 2

This example illustrates the preparation of poly(2,2'-di-
20 nitro-4,4'-biphenylene)-o,o'-dinitro-p,p'-biphenylene di-
carboxamide and the preparation therefrom of birefringent
polymeric films.

A 50 ml reaction vessel (a resin-making kettle equipped
with a mechanical stirrer, nitrogen inlet tube and calcium
25 chloride drying tube) was heated while simultaneously
flushing the vessel with nitrogen. After the reaction
vessel had cooled to room temperature, 1.5 g of anhydrous
lithium chloride and 0.4799 g (0.001750 mole) of re-

reaction vessel was fitted with a rubber
stopple and 30 ml of anhydrous distilled N-methylpyrrol-
idone (NMP) and 20 ml of anhydrous distilled tetramethyl-

1 The resulting mixture was stirred and warmed to 40°C until all solids had dissolved. The solution was then cooled in a bath of ice and salt to a temperature of -5°C. Recrystalliz- ed colourless 2,2'-dinitro-4,4'-biphenyl dicarbonyl chloride (0.6460 g; 0.00175 mole) was quickly added by

5 means of a funnel to the stirred 2,2'-dinitrobenzidine solution. An additional 3 ml of NMP were added through the funnel to the reaction mixture. The temperature of the reaction mixture did not rise above a temperature of 0°C. After stirring for 30 minutes, there was no noticeable

10 change in reaction mixture viscosity.

The ice bath was removed from the reaction vessel and the temperature was observed to rise to 20°C in 30 minutes at which point the reaction solution was heated in stages up

15 to 90°C over a period of 2.5 hours.

The reaction product, a 3 % wt./vol. polymer solution (3 g of polymer per 100 ml of reaction solvent) was cooled to 40°C and poured into 200 ml of ice-water in a blender.

20 The resulting gelatinous solid was filtered and washed (in the blender) twice each with water, acetone and ether. The product was dried in a vacuum oven at 15 mm Hg pressure and 90°C for 18 hours. The polymeric product, obtained in 88 % yield, was a dark-yellow powder having the following re-

25 curring structural units:
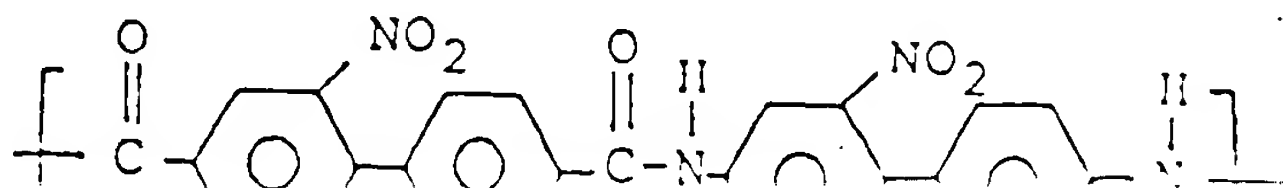
The inherent viscosity of a polymer solution (0.5 g of the polymer of Example 2 per 100 ml of

.40 dl/g at 30 °C.

Molecular structure was confirmed by infrared spectroscopy. Inspection of the ultraviolet/visible absorption spectrum for the polymer of Example 2 (in 5 % wt./vol. lithium chloride/dimethylacetamide) showed a λ_{max} of 307 nm (ε = 38,400) and an absorption peak at 365 nm (ε = 3,000).

Elemental analysis for $C_{26}H_{14}N_6O_{10}$ provided the following:

	%C	%H	%N	%O
Calculated:	54.74	2.47	14.73	28.06
Found	54.24	2.60	13.91	29.25 (by difference)

Thermogravimetric analysis showed that onset of degradation of the polymer of Example 2 occurred at 360°C in nitrogen and at 300°C in air. Differential scanning calorimetry and thermal mechanical analysis of film samples showed a reproducible transition at about 190°C.

Polymeric films were prepared from the polymeric material of Example 2 by casting (onto glass plates) a solution of the polymeric material in a 5 % wt./vol. solution of lithium chloride and dimethylacetamide (5 g lithium chloride per 100 ml of dimethylacetamide). The concentration of polymer was 5 % wt./vol., i.e., 5 g polymer per 100 ml of the lithium chloride/dimethylacetamide solution. In each instance, the glass plate carrying the puddle-cast polymer solution was immersed in water (after most of the solvent had evaporated). The polymer film was observed to gel and a

chloride and solvent.

mer films for several hours for removal of occluded lithium chloride and solvent as aforedescribed) were cut into strips. The strips were mounted between the jaws of a mechanical unidirectional stretcher. The strips were stretched (in boiling ethylene glycol) to about 60 % elongation, to effect film orientation. The resulting polymeric strips were optically transparent. Birefringence, measured with the aid of a quartz wedge, and by index matching, was 0.33. The calculated isotropic refractive index was 1.75. Wide-angle X-ray analysis of·the birefringent films showed crystallinity to be less .than 10 % by weight.

Example 3

This example illustrates the preparation of poly(2,2'-dibromo-4,4'-biphenylene)-o,o'-dibromo-p,p'-biphenylene dicarboxamide and the preparation therefrom of birefringent polymeric films.

A 50 ml reaction vessel (a resin-making kettle equipped with a mechanical stirrer, nitrogen inlet tube and calcium chloride drying tube) was heated while simultaneously flushing the vessel with nitrogen. After the reaction vessel had cooled to room temperature, 2.0 g of anhydrous lithium chloride and 0.7828 g (0.002289 mole) of sublimed 2,2'-dibromobenzidine were added while maintaining a positive nitrogen pressure. The reaction vessel was fitted with a thermometer and a rubber stopple and 20 ml of anhydrous

... aid of syringes. The resulting mixture was stirred and warmed to 40°C until all solids had dissolved. The solution was then cooled in a bath of ice and salt ... temperatur... carbonyl chloride (1.0000 g; 0.002289 mole) was quickly

1   added by means of a funnel to the stirred 2,2'-dibromobenz-
idine solution. An additional 5 ml of TMU, at a temperature
of 25°C, were added through the funnel to the reaction
mixture. The temperature of the reaction mixture rose to
15°C and then dropped to 4°C. After stirring for 15 minutes,
5   the reaction mixture began to thicken and streaming bire-
fringence (but not stir opalescence) was observed. Stirring
was continued for an additional 30 minutes at 7°C and the
ice bath was removed from the reaction vessel. The temper-
ature of the reaction mixture rose to 25°C (in 90 minutes)
10   and the reaction mixture was then slowly heated to 100°C
over a two-hour period.

The reaction product, a 4 % wt./vol. polymer solution
(4 g of polymer per 100 ml of reaction solvent) was cooled
15   to 40°C and poured into 200 ml of ice-water in a blender.
The resulting fibrous solid was filtered and washed (in
the blender) twice each with water, acetone and ether. The
product was dried in a vacuum oven at 15 mm pressure and
90°C for 18 hours. The product, obtained in 96.6 % yield,
20   was a white fibrous polymeric material having the following
recurring structural units:

25
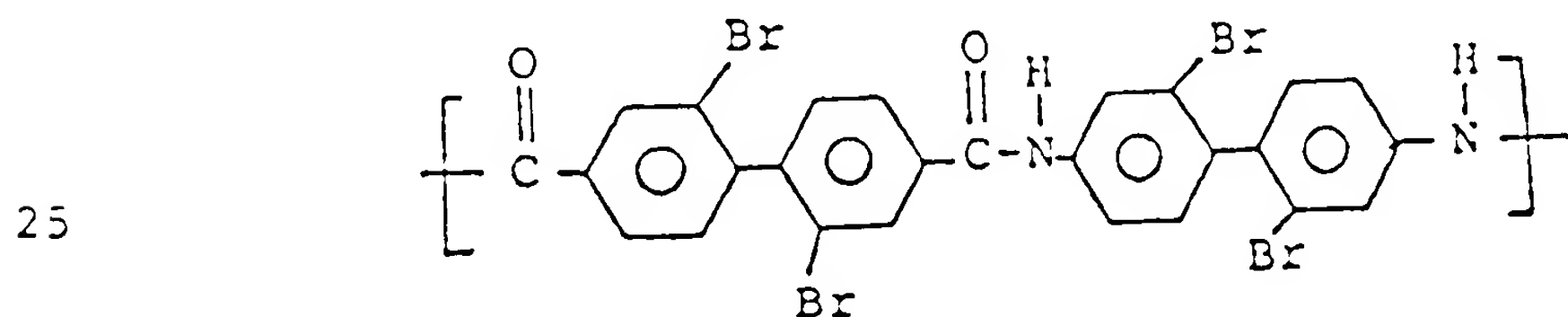
2.04 dl/g at 30 °C. Molecular weight determination based
on light scattering, indicated 2.72 x 10^5, and by gel

1   Inspection of the ultraviolet/visible absorption spectrum
for the polymer of Example 3 (in 5 % wt./vol. lithium
chloride/dimethylacetamide) showed a λ_{max} of 305 nm
(ε = 31,900) and no absorption above 380 nm.

5   Elemental analysis for $C_{26}H_{14}Br_4N_2O_2$ provided the following:

	%C	%H	%Br	%N	%O
Calculated:	44.23	1.99	45.27	3.99	4.52
Found:	44.54	2.19	45.25	3.87	4.15

10

Thermogravimetric analysis showed that onset of degradation
of the polymer of Example 3 occurred at 530°C in nitrogen.
Thermal mechanical analysis of film samples showed a re-
producible transition at about 120°C.

15

Polymeric films were prepared from the polymeric material
of Example 3 by casting (onto glass plates) solutions of
the polymeric material in a 5 % wt./vol. solution of
lithium chloride and dimethylacetamide (5 g lithium
20   chloride per 100 ml of dimethylacetamide). The concentration
of polymer ranged from 0.5 to 5 % wt./vol., i.e. from 0.5 g
to 5 g polymer per 100 ml of the lithium chloride/dimethyl-
acetamide solution. In each instance, the glass plate
carrying the puddle-cast polymer solution was immersed in
25   water (after most of the solvent had evaporated). The poly-
mer film was observed to gel and a transparent, colourless
unoriented film separated from the glass plate. The result-
ing film was soaked for several hours in water to effect
extraction of occluded lithium chloride and solvent, soaked

Stretched polymeric films were prepared in the following

polymer films for several hours for removal of occluded
lithium chloride and solvent as aforedescribed) were cut
into strips. The strips were mounted for stretching between
the jaws of a mechanical unidirectional stretcher. Strips
were stretched, in some instances, in air at 220°C and, in

5   other instances, in boiling ethylene glycol. Elongation
ranged from 60 % to 65 %. Infrared dichroism indicated that
the films were less than 65 % oriented. The films were
optically transparent. Birefringence, measured with the aid
of a quartz wedge, was 0.390. Wide-angle X-ray analysis of

10 the birefringent polymer films showed them to be less than
10 % by weight crystalline.

Example 4

15 This example illustrates the preparation of poly(2,2'-di-
chloro-5,5'-dimethoxy-biphenylene)-o,o'-dibromo-p,p'-bi-
phenylene dicarboxamide and the preparation therefrom of
birefringent polymeric films.

20 A 50-ml reaction vessel (a resin-making kettle equipped with
a mechanical stirrer, nitrogen inlet tube and calcium
chloride drying tube) was heated while simultaneously
flushing the vessel with nitrogen. After the reaction vessel
had cooled to room temperature, 1.5 g of anhydrous lithium

25 chloride and 0.6519 g (0.002082 mole) of sublimed 2,2'-di-
chloro-5,5'-dimethoxybenzidine were added while maintaining
a positive nitrogen pressure. The reaction vessel was fitted
with a thermometer and a rubber stopple and 10 ml of an-

added with the aid of syringes. The resulting mixture was
stirred and warmed to 40°C until all solids had dissolved.

lithium chloride precipitation was observed. Recrystallized

2,2'-dibromo-4,4'-biphenyldicarbonyl chloride (0.9095 g; 0.002082 mole) was quickly added by means of a funnel to the stirred 2,2'-dichloro-5,5'-dimethoxybenzidine solution. An additional 10 ml of TMU (at a temperature of 25°C) were added through the funnel to the reaction mixture. The temperature of the reaction mixture did not rise above a temperature of 0°C. After stirring for 30 minutes, the formation of a gelatinous, light-yellow, transparent mass (which exhibited streaming brefringence but not stir opalescence) was observed. Stirring was continued for an additional 10 minutes at 8°C, the stirring was stopped and the ice bath was removed. The temperature of the reaction mass was observed to rise to 25°C in 15 minutes, and the gel became stiffer in consistency. Heating was immediately commenced and an additional 20 ml of TMU were added to facilitate dissolution of the reaction mass. Within 60 minutes the temperature rose to 90°C and the gel melted to provide a homogeneous, viscous solution. Heating at 90°C was continued for two hours while stirring vigorously.

The reaction product, a 2.82 % wt./vol. light-yellow polymer solution (2.82 g of polymer per 100 ml of reaction solvent) was cooled to 40°C and the resulting gelatinous, transparent mass was added to 200 ml of ice-water in a blender. The resulting rubbery solid was filtered and washed (in the blender) twice each with water, acetone and ether. The product was dried in a vacuum oven at 15 mm Hg pressure and 90°C for 18 hours. The product, obtained in 99.3 % yield, was a very pale-yellow fibrous polymeric
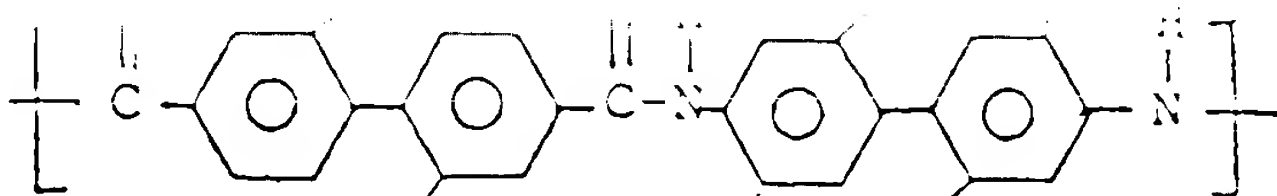
The inherent viscosity of a polymer solution (0.5 g of the polymer of Example 4 per 100 ml of a solution of 5 g lithium chloride per 100 ml of dimethylacetamide) was 5.75 dl/g at 30°C.

Molecular structure was confirmed by infrared spectroscopy. Elemental analysis for $C_{28}H_{18}Br_2Cl_2N_2O_4$ provided the following:

	%C	%H	%Br	%Cl	%N	%O
Calculated:	49.66	2.68	23.60	10.47	4.14	9.45
Found:	49.05	2.95	23.07	--	4.15	--

Polymeric films were prepared from the polymeric material of Example 4 by casting (onto glass plates) solutions of the polymeric material in a 5 % wt./vol. solution of lithium chloride and dimethylacetamide (5 g lithium chloride per 100 ml of dimethylacetamide). The concentration of polymer was 2 % wt./vol., i.e., 2 g of polymer per 100 ml of the lithium chloride/dimethylacetamide solution. In each instance, the glass plate carrying the puddle-cast polymer solution was immersed in water (after minimal evaporation of solvent). The polymer film was observed to gel and a transparent, colourless unoriented film separated from the glass plate. The resulting film was soaked for 2 days in water to effect extraction of occluded lithium chloride and solvent, soaked in acetone and dried in a vacuum oven at 90°C and 15 mm pressure. Refractive index, measured by interferometry was 1.87.

mer films for several hours for removal of occluded lithium chloride and solvent as aforedescribed) were cut

1 mounted between the jaws of a mechanical unidirectional
stretcher. The strips were stretched (in air at 220°C) to
about 50 % elongation, to effect film orientation. The
stretched films were optically transparent. Birefringence,
measured with the aid of a quartz wedge, was 0.24.

5

Solutions of the polymer of Example 4, in a concentration
of 3 to 5 % wt./vol., in lithium chloride-containing
solvents (e.g., dimethylacetamide containing lithium
chloride) were found to form colourless, transparent gels
10 which could be melted and resolidified without thermal
degradation. When the molten solutions were poured into
molds or cast into films, solidification was rapid and the
solid pieces or films were readily removable. The resulting
rubbery solids exhibited high birefringence upon application
15 of very slight stress. Removal of the stress was accompanied
by instantaneous disappearance of the birefringent property.

Example 5

20 This example illustrates the preparation of poly(2,2'-di-
bromo-4,4'-biphenylene)-octafluoro-p,p'-biphenylene di-
carboxamide and the preparation therefrom of birefringent
polymeric films.

25 A 50-ml reaction vessel (a resin-making kettle equipped
with a mechanical stirrer, nitrogen inlet tube and calcium
chloride drying tube) was heated while simultaneously
flushing the vessel with nitrogen. After the reaction
vessel had cooled to room temperature, 1.5 g of anhydrous

with a thermometer and a rubber stopple and 10 ml of an-
hydrous distilled N-methylpyrrolidone (NMP) and 10 ml of

added with the aid of syringes. The resulting mixture was
stirred and warmed to 40°C until all solids had dissolved.
The solution was then cooled in a bath of ice and salt to
a temperature of 0°C. A small amount of lithium chloride
precipitation was observed. Distilled 2,2',3,3',5,5',6,6'-
octafluoro-4,4'-biphenylene dicarbonyl chloride (0.5660 g;
0.001338 mole) was quickly added by means of a funnel to
the stirred, 2,2'-dibromobenzidine solution. An additional
10 ml of TMU (at a temperature of 25°C) were added through
the funnel to the reaction mixture. The temperature of the
reaction mixture did not rise above a temperature of 2°C.
After stirring for 15 minutes, the reaction mixture began
to thicken and streaming birefringence (but not stir
opalescence) was observed. Stirring was continued for an
additional 30 minutes at 4°C and the ice bath was removed.
The temperature of the reaction mixture was observed to
rise to 25°C in 40 minutes at which point the reaction
solution was slightly viscous and cloudy in appearance.
The reaction mixture was warmed gently for 90 minutes with
stirring. The temperature of the reaction mixture rose
during the warming to a maximum temperature of 45°C at
which temperature the reaction solution became homogeneous.
Stirring was continued for 18 hours at 45°C.

The resulting reaction product, a 3 % wt./vol. polymer
solution (3 g of polymer per 100 ml of reaction solvent)
was cooled to 40°C and poured into 200 ml of ice-water in
a blender. The resulting fibrous solid was filtered and
washed (in the blender) twice each with water, acetone and

having the following recurring structural units:
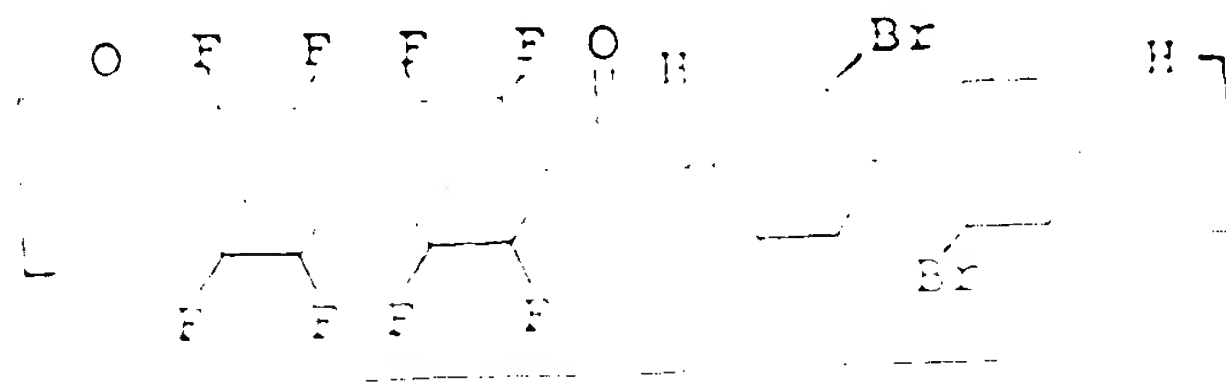
1 The inherent viscosity of a polymer solution (0.5 g of the
polymer of Example 5 per 100 ml of a solution of 5 g
lithium chloride per 100 ml of dimethylacetamide) was
1.68 dl/g at 30°C.

5 Molecular structure was confirmed by infrared spectroscopy.
Inspection of the ultraviolet/visible absorption spectrum
for the polymer of Example 5 (in 5 % wt./vol. lithium
chloride/dimethylacetamide) showed a λ_{max} of 340 nm and an
absorption peak at 360 nm (ε = 306).

10 Elemental analysis for $C_{26}H_8Br_2F_8N_2O_2$ provided the follow-
ing:

	%C	%H	%Br	%F	%N	%O
Calculated:	45.11	1.17	23.09	21.97	4.05	4.61
Found:	42.89	1.17	21.86	20.81	3.76	9.51 (by difference)

Thermogravimetric analysis showed that onset of degradation
of the polymer of Example 5 occurred at 325°C in nitrogen

20 and at 350°C in air. Differential scanning calorimetry
showed a reproducible transition at about 155°C.

Polymeric films were prepared from the polymeric material
of Example 5 by casting (onto glass plates) solutions of

25 the polymeric material in a 2 % wt./vol. solution of
lithium chloride and dimethylacetamide (2 g lithium
chloride per 100 ml of dimethylacetamide). The concentration
of polymer ranged from 0.5 to 5 % wt./vol., i.e., from
0.5 g to 5 g polymer per 100 ml of the lithium chloride/

30 dimethylacetamide solution. In each instance, the glass

The polymer was observed to gel and a transparent and
colourless unoriented film separated from the glass plate.

effect extraction of occluded lithium chloride and solvent, soaked in acetone and dried in a vacuum oven at 90°C and 15 mm Hg pressure. Refractive index, measured by interferometry was 1.74.

Stretched polymeric films were prepared in the following manner. Water-swollen films (obtained by soaking the polymer films for several hours for removal of occluded lithium chloride and solvent as aforedescribed) were cut into strips. The strips were mounted between the jaws of a mechanical unidirectional stretcher. The strips were oriented by stretching (in air at 200°C) to an elongation in the range of 50 to 55 %. The polymeric strips were optically transparent. Birefringence, measured with the aid of a quartz wedge, was 0.35. Strips were also stretched in methanol at 25°C to an elongation of 55 %. Measurement of birefringence for such stretched films showed a birefringence of 0.44.

Example 6

This example illustrates the preparation of poly(2,2',3,3', 4,4',6,6'-octafluoro-4,4'-biphenylene) carbohydrazide and the preparation therefrom of birefringent polymeric films.

A 50-ml reaction vessel (a resin-making kettle equipped with a mechanical stirrer, nitrogen inlet tube and calcium chloride drying tube) was heated while simultaneously flushing the vessel with nitrogen. After the reaction

. . . . of anhydrous

positive nitrogen pressure. The reaction vessel was fitted with a thermometer and a rubber stopple and 7 ml

of anhydrous distilled tetrahydrofuran

1 added with the aid of syringes. The resulting mixture was stirred until most of the lithium chloride had dissolved. The solution was then cooled in a bath of ice and salt to a temperature of 0°C. A small amount of lithium chloride precipitation was observed. Distilled 2,2',3,3',5,5',6,6'-

5 octafluoro-4,4'-biphenylene dicarbonyl chloride (0.5100 g; 0.001205 mole) was quickly added by means of a funnel to the stirred hydrazine solution. An additional 4 ml of TMU (at a temperature of 25°C) were added through the funnel to the reaction mixture. The temperature of the reaction mixture

10 did not rise above a temperature of 5°C. The reaction mixture did not thicken and streaming birefringence was not observed. Lithium carbonate (0.0890 g; 0.0024 mole) was added to the reaction mixture, stirring was continued for 30 minutes at 4°C and the ice bath was removed. As the

15 temperature of the reaction mixture rose to 25°C during the subsequent 60 minutes, the reaction solution first became cloudy and, then, a white precipitate formed. Over the next 30 minutes, the reaction mixture was warmed to 40°C at which time the reaction mixture became homogeneous.

20 The reaction temperature was raised to 70°C and maintained for 1 hour. No increase in viscosity was apparent.

The reaction product, a 1.99 % wt./vol. polymer solution (1.99 g of polymer per 100 ml of reaction solvent) was

25 cooled to 40°C and poured into 200 ml of ice-water in a blender. The resulting powdery solid was filtered and washed (in the blender) twice each with water, acetone and ether. The product was dried in a vacuum oven at 15 mm Hg pressure and 90°C for 18 hours. The polymeric product,

30 obtained in 95.4 % yield, was a white solid material having
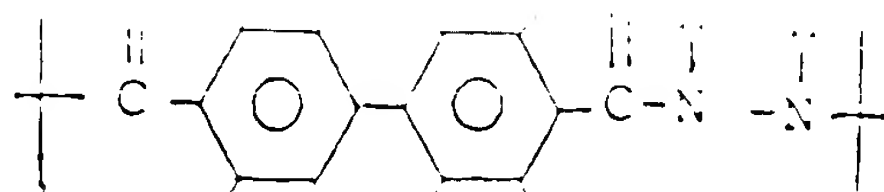
The inherent viscosity of a polymer solution (0.5 g of the polymer of Example 6 per 100 ml of a solution of 5 g lithium chloride per 100 ml of dimethylacetamide) was 1.16 dl/g at 30°C. The molecular structure of the polymer of Example 6 was confirmed by infrared spectroscopy.

Polymeric films were prepared from the polymeric material of Example 6 by casting (onto glass plates) solutions of the polymeric material in a 2 % wt./vol. solution of lithium chloride and dimethylacetamide (2 g lithium chloride per 100 ml of dimethylacetamide). The concentration of polymer ranged from 0.5 to 5 % wt./vol., i.e., from 0.5 g to 5 g polymer per 100 ml of the lithium chloride/ dimethylacetamide solution. In each instance, the glass plate carrying the puddle cast polymer solution was immersed in water (after evaporating the solvent for 1 hour). The polymer film was observed to gel, and a physically weak, cloudy and colourless film separated from the glass plate. The resulting film was soaked for several hours in water to effect extraction of occluded lithium chloride and solvent, soaked in acetone and dried in a vacuum oven at 90°C and 15 mm pressure. The films were not of sufficient strenth to undergo stretching. Refractive index, measured by interferometry, was 1.60.

Example 7

This example illustrates the preparation of poly(2,2'-di-bromo-4,4'-biphenylene)-trans-p,p'-stilbene dicarboxamide

A 250-ml reaction vessel (a resin-making kettle equipped with a mechanical stirrer, nitrogen inlet tube and calcium

1   vessel had cooled to room temperature, 4.88 g of anhydrous
lithium chloride and 2.1441 g (0.006269 mole) of sublimed
2,2'-dibromobenzidine were added while maintaining a
positive nitrogen pressure. The reaction vessel was fitted
with a thermometer and a rubber stopple and 45 ml of an-

5   hydrous distilled N-methylpyrrolidone (NMP) and 45 ml of
anhydrous distilled tetramethylurea (TMU) were carefully
added with the aid of syringes. The resulting mixture was
stirred and warmed to 40°C until all solids had dissolved.
The solution was then cooled in a bath of ice and salt to

10   a temperature of -5°C. A small amount of lithium chloride
precipitation was observed. Recrystallized trans-p,p'-
stilbene dicarbonyl chloride (1.9129 g; 0.006269 mole) was
quickly added by means of a funnel to the stirred 2,2'-di-
bromobenzidine solution. An additional 30 ml of NMP/TMU

15   mixture (1:1 by weight), at a temperature of 25°C, were
added through the funnel to the reaction mixture. The
temperature of the reaction mixture did not rise above a
temperature of 5°C and then dropped rapidly to -3°C. After
stirring for 30 minutes, the reaction mixture began to

20   thicken and streaming birefringence (but not stir opales-
cence) was observed. Lithium carbonate (0.926 g,
0.01254 mole) was added and stirring was continued for an
additional 30 minutes at 0°C.

25   The ice bath was removed from the reaction vessel, and when
the temperature reached 20°C (in 30 minutes), the reaction
solution had become sufficiently viscous as to begin to
climb the shaft of the mechanical stirrer. A maximum
reaction temperature of 55°C was reached. Stirring was
stopped and the mixture was heated overnight at a temper-

per 100 ml of reaction solvent) was diluted with 100 ml of
2 % wt./vol. lithium chloride in dimethylacetamide. The

1 and water in a blender. The resulting fibrous solid was
filtered and washed (in the blender) twice each with water,
acetone and ether. The product was dried in a vacuum oven
at 15 mm Hg pressure and 90°C for 18 hours. The polymeric
product, obtained in 100 % yield, was a very light-yellow
5 fibrous solid having the following recurring structural
units:

10
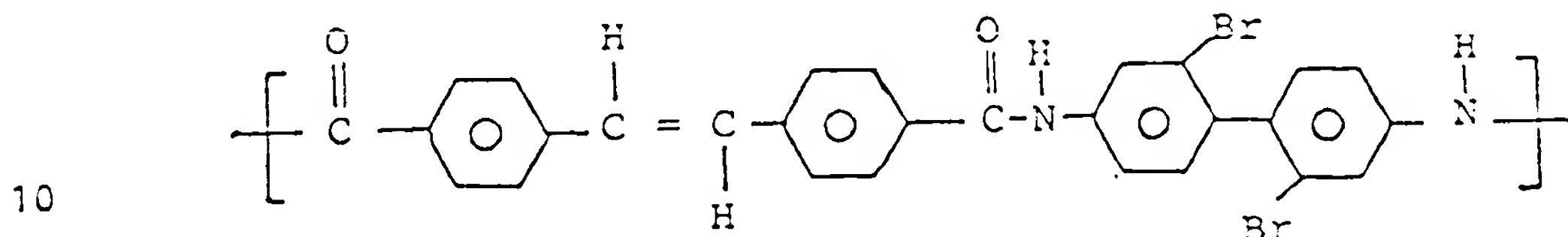
The inherent viscosity of a polymer solution (0.5 g of the
polymer of Example 7 per 100 ml of a solution of 5 g
15 lithium chloride per 100 ml of dimethylacetamide) was 9.04
dl/g at 30°C. The molecular weight of the polymer, as
determined by light scatterings, was 1.95×10^6, and by
gel permeation chromatography, 8.71×10^5.

20 The molecular structure of the polymer was confirmed by
infrared spectroscopy. Inspection of the ultraviolet/
visible spectrum of the polymer (in 5 % wt./vol. lithium
chloride/dimethylacetamide) showed a λ_{max} of 352 nm
($\varepsilon = 66,000$); an absorption peak at 368 nm ($\varepsilon = 52,800$)
25 and an extremely weak tail at 400 nm.

Elemental analysis for $C_{28}H_{18}Br_2N_2O_2$ provided the follow-
ing:

1   in nitrogen and at 515°C in air. Differential scanning
calorimetry and thermal mechanical analysis of film samples
detected a reproducible transition at about 225°C.

Polymeric films were prepared from the polymeric material
5   of Example 7 by casting (onto glass plates) solutions of
the polymeric material in a 5 % wt./vol. solution of
lithium chloride and dimethylacetamide (5 g lithium
chloride per 100 ml of dimethylacetamide). The concentrat-
ion of polymer ranged from 1 to 5 % wt./vol., i.e., from
10   1 g to 5 g polymer per 100 ml of the lithium chloride/
dimethylacetamide solution. In each instance, the glass
plate carrying the puddle-cast polymer solution was
immersed in water (after minimal evaporation of solvent).
The polymer was observed to gel and a transparent and
15   colourless unoriented film separated from the soaked glass
plate. The resulting film was soaked for several hours
in water to effect extraction of occluded lithium chloride
and solvent, soaked in acetone and dried in a vacuum oven
at 90°C and 15 mm Hg pressure. Refractive index, measured
20   by interferometry, was 2.03.

Stretched polymeric films were prepared in the following
manner. Water-swollen films (obtained by soaking the poly-
mer films for several hours for removal of occluded
25   lithium chloride and solvent as aforedescribed) were cut
into strips. The strips were mounted between the jaws of
a mechanical unidirectional stretcher. The strips were
stretched (in air at 220°C) to about 55 to 55 % elongation,
to effect film orientation. The stretched films were

... modulus was ... x 10 Kg/m². Wide-angle X-ray analysis
of the films showed crystallinity to be less than 10 % by
weight. Birefringence ...

Solutions of the polymer of Example 7 in lithium chloride/
dimethylacetamide, as aforedescribed, were formed into
extruded films by the "wet-jet" method whereby the solution
of polymer is extruded into an aqueous coagulation bath for
gelling of the polymer material. The resulting transparent,
colourless film strips were soaked in water and cut to
about 25.4 to 50.8 mm for testing. The partially oriented
strips of film produced by the extrusion were further
oriented by stretching in the manner described in the
Examples hereof. Stretching was effected in air at a
temperature of 180°C. Elongation was to the break point,
in the range of about 40 % to 50 %. The stretched strips
were optically transparent. Infrared dichroism indicated
that the films were 85 % oriented. Measurement of bire-
fringence utilizing a quartz wedge provided a birefringence
value of 0.977. Measurement by resort to interferometry
provided a value of 0.865.

Example 8

This example illustrates the preparation of poly(2,2'-di-
bromo-4,4'-biphenylene)-trans-α-bromo-biphenylene dicarb-
oxamide and the preparation therefrom of birefringent
polymeric films.

A 50-ml reaction vessel (a resin-making kettle equipped
with a mechanical stirrer, a pressure-equalizing dropping
funnel, a nitrogen inlet tube and calcium chloride drying
tube) was heated while simultaneously flushing the vessel

0.4779 g (0.00153 mole) of substance .....
were added while maintaining a positive nitrogen pressure.
..... was fitted with a thermometer and a
pyrrolidone (NMP) and 5 ml of anhydrous .....

methylurea (TMU) were carefully added with the aid of syringes. The resulting mixture was stirred and warmed to 40°C until all solids had dissolved. The solution was then cooled in a bath of ice and salt to a temperature of 0°C. A small amount of lithium chloride precipitation was ob-
served. Recrystallized α-bromo-p,p'-stilbene dicarbonyl chloride (0.5366 g; 0.001397 mole) was quickly added by means of a funnel to the stirred 2,2'-dibromobenzidine solution. An additional 10 ml of TMU (at a temperature of 25°C) were added through the funnel to the reaction mixture. The temperature of the reaction mixture did not rise above a temperature of 4°C. After stirring for 15 minutes, the reaction mixture began to thicken and streaming bire-fringence (but not stir opalescence) was observed. Stirring was continued for an additional 30 minutes at 4°C.

The ice bath was removed from the reaction vessel and the temperature was observed to rise to 25°C in 90 minutes at which point the reaction mixture had become sufficiently viscous as to climb the shaft of the mechanical stirrer. Over the next 90 minutes, the very pale-yellow reaction mass was gently warmed with intermittent stirring; the maximum temperature reached was approximately 70°C.

The reaction product, a 3 % wt./vol. polymer solution (3 g of polymer per 100 ml of reaction solvent) was cooled to 40°C and poured into 200 ml of ice-water in a blender. The resulting fibrous solid was filtered and washed (in the blender) twice each with water, acetone and ether. The product was dried in a vacuum oven at 15 mm Hg pressure and
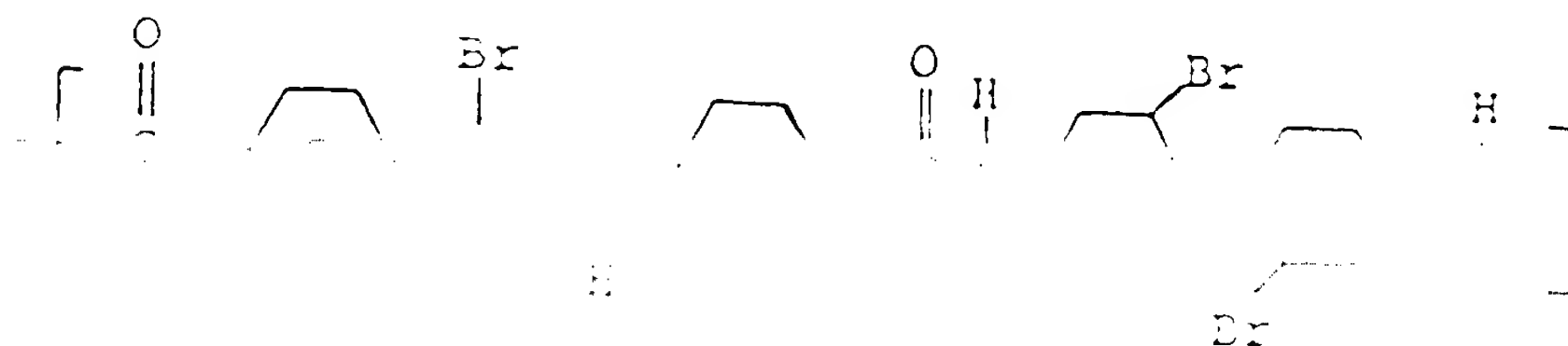
The inherent viscosity of a polymer solution (0.5 g of the polymer of Example 8 per 100 ml of a solution of 5 g lithium chloride per 100 ml of dimethylacetamide) was 7.81 dl/g at 30°C.

Molecular structure was confirmed by infrared spectroscopy. Elemental analysis for $C_{28}H_{17}N_2Br_3O_2$ provided the following:

	%C	%H	%Br	%N	%O
Calculated:	51.478	2.604	36.724	4.289	4.90
Found:	51.17	2.80	34.92	4.15	7.06 (by difference)

Polymeric films were prepared from the polymeric material of Example 8 by casting (onto glass plates) solutions of the polymeric material in a 5 % wt./vol. solution of lithium chloride and dimethylacetamide (5 g lithium chloride per 100 ml of dimethylacetamide). The concentration of polymer ranged from 0.5 to 5 % wt./vol., i.e., from 0.5 g to 5 g polymer per 100 ml of the lithium chloride/dimethylacetamide solution. In each instance, the glass plate carrying the puddle-cast polymer solution was immersed in water (after minimal evaporation of solvent). The polymer was observed to gel and a transparent and colourless unoriented film separated from the soaked glass plate. The resulting film was soaked for several hours in water to effect extraction of occluded lithium chloride and solvent, soaked in acetone and dried in a vacuum oven at 90°C and 15 mm Hg pressure Refractive index, measured by interferometry, was 2.07.

polymer films for several hours in lithium chloride and solvent as aforedescribed) were cut into strips. The strips were mounted between the jaws of a

stretched (in air at 220°C) to about

1   to effect film orientation. The stretched strips were
     optically transparent. Birefringence, measured with the aid
     of a quartz wedge, was 0.680.

     Solutions of the polymer of Example 8 in lithium chloride/
5   dimethylacetamide, as aforedescribed, were formed into ex-
     truded films by the "wet-jet" method whereby the solution
     of polymer is extruded into an aqueous coagulation bath for
     gelling of the polymer material. The resulting transparent,
     colourless film strips were soaked in water and cut to
10   about 25.4 to 50.8 mm for testing. The partially oriented
     strips of film produced by the extrusion were further
     oriented by stretching in the manner described in the
     Examples hereof. Stretching was effected in air (at a
     temperature of 180°C) to the break point, in the range of
15   about 40 % to 50 % elongation. The stretched film strips
     were otpically transparent. Measurement of birefringence
     utilizing a quartz wedge provided a birefringence value of
     0.955. Measurement by resort to interferometry provided a
     value of 0.849.

20

Example 9

     This example illustrates the preparation of poly(2,2'-di-
     bromo-4,4'-biphenylene)-α,α'-dimethylmuconamide and the
25   preparation therefrom of birefringent polymeric films.

     A 50-ml reaction vessel (a resin-making kettle equipped with
     a mechanical stirrer, a pressure-equalizing dropping funnel,
     a nitrogen inlet tube and calcium chloride drying

     ... g of anhydrous lithium chloride and 0.8519 g (0.00249
   mole) of sublimed 2,2'-dibromo-benzidine were added while
     maintaining a positive

of anhydrous distilled N-methylpyrrolidone (NMP) were carefully added with the aid of a syringe. The resulting mixture was stirred and warmed to 40°C until all solids had dissolved. The solution was then cooled in a bath of ice and salt to a temperature of 0°C with formation of some lithium chloride precipitate. A solution of recrystallized α,α'-dimethyl muconyl chloride (0.5157 g; 0.002491 mole) in 6 ml of anhydrous, distilled tetrahydrofuran (THF) was added to the dropping funnel through a rubber stopper with a syringe. The α,α'-dimethyl muconyl chloride/THF solution, the temperature of which was 25°C, was added dropwise over 5 minutes to the cold 2,2'-dibromobenzidine solution while stirring moderately. The addition funnel was rinsed with 6 ml of NMP which was also added dropwise to the reaction mixture in order to prevent the temperature of the reaction mixture from rising above 1°C. After stirring for 1 hour, during which time the solution turned lemon-yellow (but did not thicken), 0.354 g of solid lithium carbonate was added all at once to the reaction mixture. Within 10 minutes noticeable thickening was observed, and after an additional 20 minutes, at 20°C, the viscosity increased further. The ice bath was removed from the reaction vessel and the temperature of the reaction mixture was allowed to rise to 25°C over a one-hour period during which time a thick paste had formed. The temperature of the reaction mixture was increased to 65°C over the next 20 minutes producing a mixture which could no longer be stirred. Additional heating for 18 hours at 55°C without stirring produced a trans-light-yellow viscous polymer solution. The reaction

considerable streaming-birefringence under mild mechanical stress; stir opalescence was not, however,

The polymer solution was poured into a blender with 200 ml of ice-water and the resulting fibrous solid was

filtered and washed (in the blender) twice each with water, acetone and ether. The product was dried in a vacuum oven at 15 mm Hg pressure and 90°C for 18 hours. The product, obtained in 94.7 % yield, was a white fibrous polymeric material having the following recurring structural units:
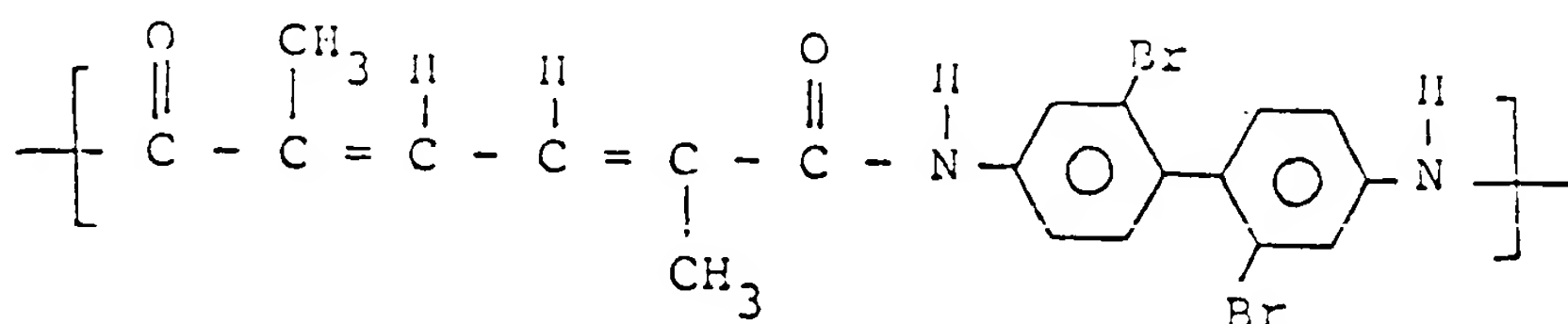
The inherent viscosity of a polymer solution (0.5 g of the polymer of Example 9 per 100 ml of a solution of 5 g lithium chloride per 100 ml of dimethylacetamide) was 4.69 dl/g at 30°C.

Molecular structure was confirmed by infrared sprectroscopy. Inspection of the ultraviolet/visible absorption spectrum for the polymer of Example 9 (in 3 % wt./vol. lithium chloride/dimethylacetamide showed a λ_{max} of 333 nm (ε = 33,600) and an extremely weak tail at 400 nm.

Elemental analysis for $C_{20}H_{16}Br_2N_2O_2$ provided the following:

	%C	%H	%Br	%N	%O
Calculated:	50.448	3.387	33.562	5.883	6.72
Found:	50.09	3.45	34.17	5.72	6.57 (by difference

Thermogravimetric analysis showed that the onset of degradation occurred at 360°C in air, with a peak rate of

at about 185°C.

1   polymeric material in a 5 % wt./vol. solution of lithium
chloride and dimethylacetamide (5 g lithium chloride per
100 ml of dimethylacetamide). The concentration of polymer
ranged from 2 to 4 % wt./vol., i.e., from 2 g to 4 g polymer
per 100 ml of the lithium chloride/dimethylacetamide solut-

5 ion. In each instance, the glass plate carrying the puddle-
cast polymer solution was immersed in water (after minimal
evaporation of solvent). The polymer film was observed to
gel and a transparent and colourless unoriented film
separated from the glass plate. The resulting film was soaked

10 for several hours in water to effect extracttion of occluded
lithium chloride and solvent, soaked in acetone and dried in
a vacuum oven at 90°C and 15 mm Hg pressure. Refractive
index, measured by interferometry, was 1.91.

15 Stretched polymeric films were prepared in the following
manner. Water-swollen films (obtained by soaking the poly-
mer films for several hours for removal of occluded lithium
chloride and solvent as aforedescribed) were cut into strips.
The strips were mounted between the jaws of a mechanical

20 stretcher and were unidirectionally stretched, successively,
in steam, acetone and boiling ethylne glycol (all of which
function as plasticizers). The strips were stretched to an
elongation of from 35 % to 45 %. The film strips were
further elongated (up to 60%) by stretching in air at 200°C.

25 The stretched strips were optically transparent. Optical
retardation was measured with a calibrated quartz wedge; film
thickness was measured with a micrometer. Birefringence,
measured by means of a quartz wedge, was 0.40.

of the present invention, an unsubstituted polyamide was
prepared and evaluated in the following manner.

1   A solution polymerization reaction for the production of
poly(p-benzamide) was conducted in accordance with the
following reaction scheme:

5

$$O = S = N - \bigcirc - \overset{\overset{\displaystyle O}{\|}}{C} - Cl \quad + \quad LiCl \quad \xrightarrow[\text{LiOH.H}_2\text{O}]{\text{TMU}}$$

$$\left[-\overset{\overset{\displaystyle H}{|}}{N} - \bigcirc - \overset{\overset{\displaystyle O}{\|}}{C} - \right]_n$$

10
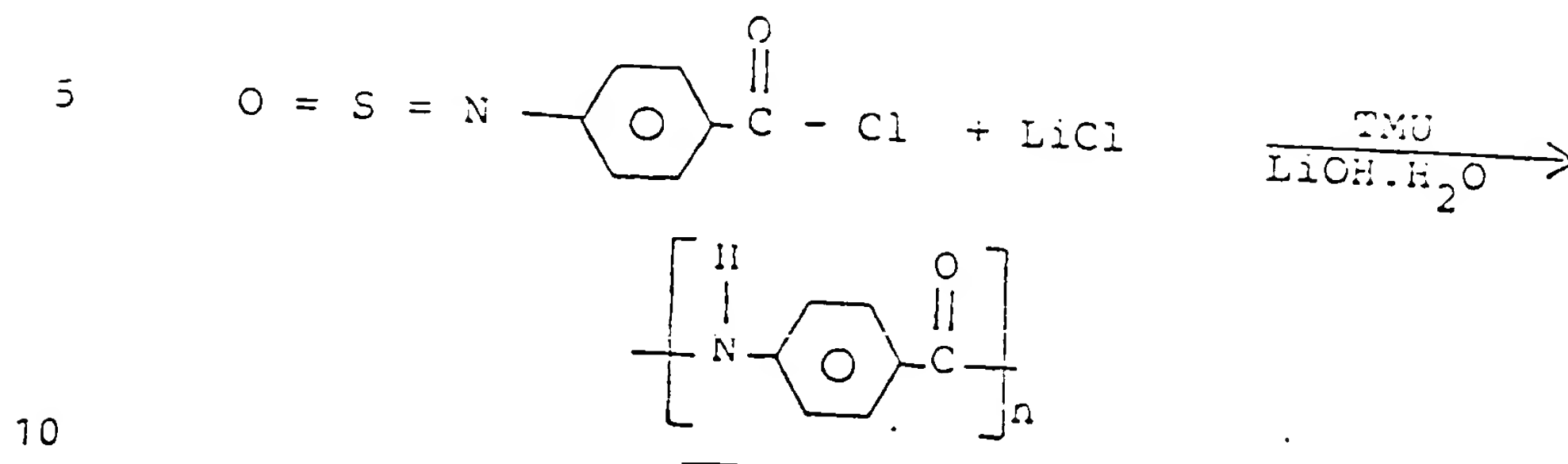
A 50-ml reaction vessel (a resin-making kettle equipped
with mechanical stirrer, nitrogen inlet tube and calcium
chloride drying tube) was heated while simultaneously
15   flushing the vessel with nitrogen. After the reaction
vessel had cooled to room temperature, 40 ml of anhydrous
distilled tetramethyl urea (TMU), 8.04 g (0.04 mole) of
vacuum-distilled p-thionylaminobenzoyl chloride and 0.52 g
(0.012 mole) of lithium chloride were added while maintain-
20   ing a positive nitrogen pressure. The resulting reaction
mixture was stirred for ten minutes at room temperature and
1.68 g (0.04 mole) of lithium hydroxide monohydrate were
added while vigorously stirring. The reaction mixture was
then stirred for 1 hour at room temperature. After a period
25   of 7 additional minutes, the reaction mixture became cloudy
and was observed to thicken. The polymeric reaction product,
after 20 minutes, thickened sufficiently to adhere the
shaft of the mechanical stirrer. After one-half hours, the
reaction mixture, which could not be stirred, was heated

... ...

... ... heated to 130°C without stirring.
After 2 hours of heating at 130°C, pliability of polymeric
reaction mass increased and the produc...

1   reaction vessel overnight and was washed with water, filtered and washed with acetone then ether. The product, poly-(p-benzamide) was dried in a vacuum oven at 80°C for 2 hours.

5   The inherent viscosity of a polymer solution of poly(p-penzamide) in sulfuric acid was 1.60 dl/g at 30°C.

    Polymeric films of poly(p-benzamide) were prepared by casting a solution of the polymeric material in a 5 % wt./
10   vol. solution of lithium chloride and dimethylacetamide (5 g lithium chloride per 100 ml of dimethylacetamide). The concentration of polymer was 5 % wt./vol., i.e., 5 g polymer per 100 ml of the lithium chloride/dimethylacetamide solution. The cast polymer film was dried in a vacuum oven
15   at 90°C overnight. The polymer film was an opaque, white flexible film. Additional films were formed by puddle-casting the solution as aforedescribed onto glass plates. In each instance, the glass plate carrying the puddle-cast polymer solution was immersed in water (after
20   most of the solvent had evaporated). The polymer film which separated from the glass plate was a tough, transparent, flexible film. The resulting film was soaked for several hours in water to effect extraction of occluded lithium chloride and solvent.

25

    Stretched polymeric films were prepared in the following manner. Water-swollen films (obtained by soaking the polymer films for several hours for removal of occluded lithium chloride and solvent as aforedescribed) were cut

were stretched to an elongation of approximately 10 %. The resulting streched films were clouded in appearance.

1 wedge; film thickness was measured with a micrometer. Birefringence, measured by means of a quartz wedge, was 0.23.

5 By inspection of the values of birefringence described in connection with the substituted polyamides of the present invention and the Examples hereof (Examples 1 to 9), it can be seen that the birefringence of poly(p-benzamide) of comparative Example 10, was, in general, decidedly lower.

Example 11

10 This example illustrates the preparation of poly-[2,2'-bis-(trifluoromethyl)-4,4'-biphenylene]-trans-p,p'-stilbene dicarboxamide and the preparation therefrom of birefringent polymeric films.

15 A 100-ml reaction vessel (a resin-making kettle equipped with a mechanical stirrer, nitrogen inlet tube and calcium chloride drying tube) was heated while simultaneously flushing the vessel with nitrogen. After the reaction vessel had
20 cooled to room temperature, 1.5 g of anhydrous lithium chloride and 0.5171 g (0.001615 mole) of recrystallized 2,2'-bis(trifluoromethyl)-benzidine were added while maintaining a positive nitrogen pressure. The reaction vessel was fitted with a thermometer and a rubber stopple and 10 ml
25 of anhydrous distilled tetramethylurea (TMU) were carefully added with the aid of syringes. The resulting mixture was stirred and warmed to 40°C until all solids had dissolved. The solution was then cooled in a bath of ice and salt to a temperature of -5°C. A small amount of lithium chloride
30 precipitation was observed. Recrystallized trans-

_____-benzidine solution. An additional 10 ml of TMU, at a temperature of 0°C, were added through the
35 funnel to the reaction mixture. _____

1   reaction mixture did not rise above a temperature of 5°C
    and then dropped rapidly to -3°C. After stirring for
    30 minutes, the reaction mixture began to thicken and
    streaming birefringence (but not stir opalescence) was
    observed. Stirring was continued for an additional
5   30 minutes at 0°C.

    The ice bath was removed from the reaction vessel, and when
    the temperature reached 20°C (in 30 minutes), the reaction
    solution had become very viscous. Over the next 75 minutes,
10 the completely colourless, transparent solution was warmed
    to 72°C. After stirring at this temperature for the next
    18 hours, the mixture was cooled to 40°C. The resulting
    polymer solution was poured into 200 ml of ice and water in
    a blender. The resulting fibrous solid was filtered and
15 washed (in the blender) twice each with water, acetone and
    ether. The product was dried in a vacuum oven at 15 mm Hg
    pressure and 90°C for 18 hours. The polymeric product,
    obtained in 99.5 % yield, was a very light-yellow fibrous
    solid having the following recurring structural units:

20

25
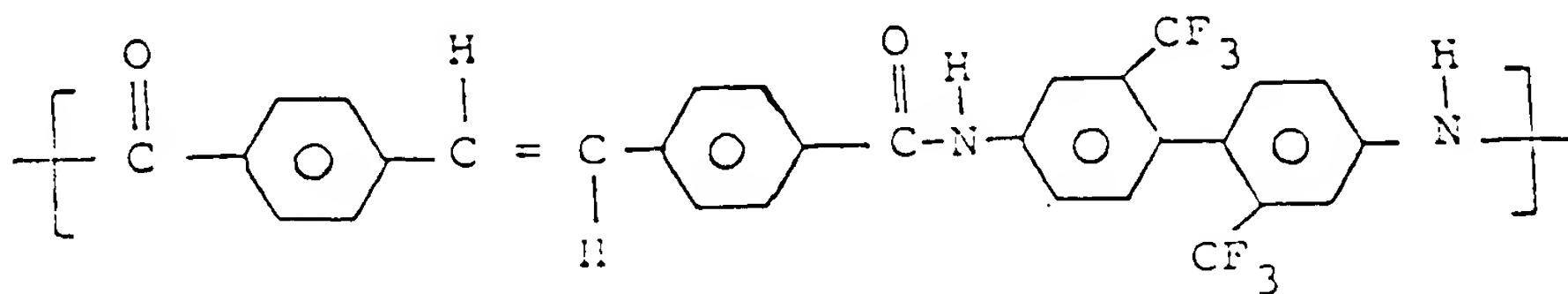
    The inherent viscosity of a polymer solution (0.5 g of the
    polymer of Example 11 per 100 ml of a solution of 5 g
    lithium chloride per 100 ml of dimethylacetamide) was

    Elemental analysis for $C_{30}H_{18}F_6N_2O_2$ provided the following:

1   Thermogravimetric analysis showed that the onset of de-
gradation of the polymer of Example 11 occurred at 500°C
in nitrogen and at 410°C in air. Differential scanning
calorimetry and thermal mechanical analysis of film samples
detected a reproducible transition at about 185°C.

5

Polymeric films were prepared from the polymeric material
of Example 11 by casting (onto glass plates) solutions of
the polymeric material in a 5 % wt./vol. solution of
lithium chloride and dimethylacetamide (5 g lithium chloride

10 per 100 ml of dimethylacetamide). The concentration of
polymer ranged from 1.0 to 5 % wt./vol., i.e., from 1.0 g
to 5 g polymer per 100 ml of the lithium chloride/dimethyl-
acetamide solution. In each instance, the glass plate
carrying the puddle-cast polymer solution was immersed in

15 water (after minimal evaporation of solvent). The polymer
film was observed to gel and a transparent and colourless
unoriented film separated from the glass plate. The result-
ing film was soaked for several hours in water to effect
extraction of occluded lithium chloride and solvent, soaked

20 in acetone and dried in a vacuum oven at 90°C and 15 mm Hg
pressure. Refractive index, measured by interferometry, was
1.997.

Stretched polymeric films were prepared in the following

25 manner. Water-swollen films (obtained by soaking the poly-
mer films for several hours for removal of occluded
lithium chloride and solvent as aforedescribed) were cut
into strips. The strips were mounted between the jaws of a
mechanical unidirectional stretcher. The strips were

30 stretched (in air at 220°C) to about 60 to 65 % elongation

35 Solutions of the polymer of Example

1 dimethylacetamide, as aforedescribed, were formed into
extruded films by the "wet-jet"method whereby the solution
of polymer is extruded into an aqueous coagulation bath
for gelling of the polymer material. The resulting tans-
parent, colourless film strips were soaked in water and
5 cut to about 25.4 to 50.8 mm for testing. The partially
oriented strips of film produced by the extrusion were
further oriented by stretching in the manner described in
the Examples hereof. Stretching was effected to an elong-
ation of less than 20 %. The stretched strips were
10 optically transparent. Infrared dichroism indicated that
the films were 92 % oriented. Measurement of birefringence
utilizing a quartz wedge provided a birefringence value of
0.879.

Example 12

15

This example illustrates the preparation of poly-[2,2'-bis-
(trifluoromethyl)-4,4'-biphenylene]-2,2'-dimethoxy-4,4'-bi-
phenyl and the preparation therefrom of birefringent poly-
20 meric films.

A 100-ml reaction vessel (a resin-making kettle equipped
with a mechanical stirrer, a pressure-equalizing dropping
funnel, a nitrogen inlet tube and calcium chloride drying
tube) was heated while simultaneously flushing the vessel
25 with nitrogen. After the reaction vessel had cooled to room
temperature, 3.0 g of anhydrous lithium chloride and
0.4328 g (0.001352 mole) of recrystallized 2,2'-bis(tri-
fluoromethyl)benzidine were added while maintaining a
_____ pressure. The reaction vessel was fitted

anhydrous distilled tetramethylurea (TMU) were _____
added with the aid of syringes. The resulting mixture was
_____ _____ _____ _____ had dissolved.

The solution was then cooled in a bath of ice and salt to a temperature of -5°C. A small amount of lithium chloride precipitation was observed. Recrystallized 2,2'-dimethoxy-4,4'-biphenyldicarbonyl chloride (0.4586 g; 0.001352 mole) was quickly added by means of a funnel to the stirred 2,2'-bis(trifluoromethyl)-benzidine solution. An additional 20 ml of TMU (at a temperature of 0°C) were added through the funnel to the reaction mixture. The temperature of the reaction mixture did not rise above a temperature of 5°C. After stirring for 30 minutes, the reaction mixture began to thicken and turned milk-like in appearance. Stirring was continued for an additional 30 minutes at 0°C.

The ice bath was removed from the reaction vessel and the temperature was observed to rise to 20°C in 30 minutes at which point the reaction mixture was viscous and opaque. Over the next 75 minutes, the opaque reaction mass was gently warmed to 40°C at which point it became transparent. After stirring at this temperature for the next 18 hours, the reaction mixture was cooled to 30°C and poured into 400 ml of ice-water in a blender. The resulting fibrous solid was filtered and washed (in the blender) twice each with water and ether. The product was dried in a vacuum oven at 15 mm Hg pressure and 90°C for 18 hours. The product, obtained in 99.3 % yield, was an off-white fibrous polymeric material exhibiting solubility in acetone or tetrahydro-furan and having the following recurring structural units:
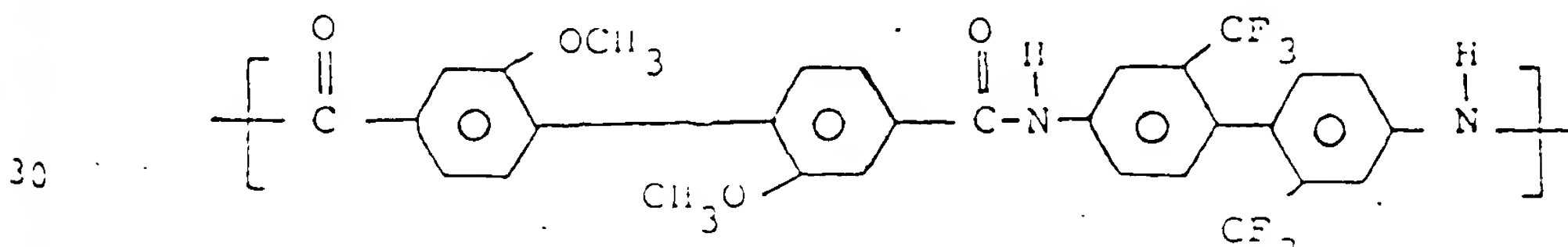
polymer of Example 12 per 100 ml of a solution of 5 g lithium chloride per 100 ml of dimethylacetamide) was

1 Molecular structure was confirmed by infrared spectroscopy. Inspection of the ultraviolet visible spectrum of the polymer (in 5 % wt./vol. lithium chloride/dimethylformamide) showed a λ_{max} of 316 nm ($\varepsilon = 2.59 \times 10^3$).

5 Elemental analysis for $C_{30}H_{20}F_6N_2O_4$ provided the following:

	%C	%H	%F	%N	%O
Calculated:	61.34	3.43	19.41	4.77	10.89
Found:	59.82	3.51	18.70	4.62	13.35 (by difference)

10 Thermogravimetric analysis showed that the onset of degradation of the polymer of Example 12 occurred at 470°C in nitrogen and at 440°C in air. Differential scanning colorimetry detected a reproducible transition at about

15 180°C.

Polymeric films were prepared from the polymeric material of Example 12 by casting (onto glass plates) solutions of the polymeric material in a 5 % wt./vol. solution of lithium chloride and dimethylacetamide (5g lithium chloride per

20 100 ml of dimethylacetamide). The concentration of polymer ranged from 1 % to 5 % wt./vol., i.e., from 1.0 g to 5 g polymer per 100 ml of the lithium chloride/dimethylacetamide solution. In each instance, the glass plate carrying the puddle-cast polymer solution was immersed in water (after

25 minimal evaporation of solvent). The polymer was observed to gel and a transparent and colourless unoriented film separated from the soaked glass plate. The resulting film was soaked for several hours in water to effect extraction of occluded lithium chloride and solvent, soaked in acetone

Solutions of the polymer of Example 12 in lithium chloride/ dimethylacetamide, as aforedescribed, were formed into

extruded films by the "wet-jet" method whereby the solution of polymer is extruded into an aqueous coagulation bath for gelling of the polymer material. The resulting transparent, colourless film strips were soaked in water and cut to about 25.4 to 50.8 mm for testing. The partially oriented strips of film produced by the extrusion were further oriented by stretching in the manner described in the Examples hereof. Stretching was effected in air (at a temperature of 180°C) to an elongation of less than 20 %. The stretched film strips were otpically transparent. Infrared dichroism indicated that the films were 92 % oriented. Measurement of birefringence utilizing a quartz wedge provided a birefringence value of 0.586.

Example 13

This example illustrates the preparation of poly[2,2',3",2"'-tetrakis(trifluoromethyl)-1,1':4',1":4",1"':4'"-quaterphenylene]-trans-p,p'-stilbenedicarboxamide and the preparation therefrom of birefringent polymeric films.

A100-ml reaction vessel (a resin-making kettle equipped with a mechanical stirrer, nitrogen inlet tube and calcium chloride drying rube) was heated while simultaneously flushing the vessel with nitrogen. After the reaction vessel had cooled to room temperature, 1.5 g of anhydrous lithium chloride and 0.5806 g (0.0009543 mole) of recrystallized 4,4"'-diamino-2,2',3",2"'-tetrakis(trifluoromethyl)1,1':4'-1":4",1"'-quaterphenyl were added while maintaining a positive nitrogen pressure. The reaction vessel was fitted with a thermometer and a rubber stopple and 10 ml of an-

added with the aid of syringes. The resulting mixture was stirred and warmed to 40°C until all solids had dissolved.

1 temperature of -5°C. A small amount of lithium chloride
precipitation was observed. Recrystallized trans-p,p'-
stilbene dicarbonyl chloride (0.2909 g; 0.0009543 mole) was
carefully added by means of a funnel to the stirred diamino-
quaterphenyl solution. An additional 10 ml of TMU, at a
5 temperature of 0°C, were added through the funnel to the
reaction mixture. The temperature of the reaction mixture
did not rise above a temperature of 7°C and then dropped
rapidly to 0°C. After stirring for 30 minutes, the reaction
mixture began to thicken and streaming birefringence (but
10 not stir opalescence) was observed. Stirring was continued
for an additonal 30 minutes 0°C.

The ice bath was removed from the reaction vessel, and when
the temperature reached 20°C (in 30 minutes), the reaction
solution had become very viscous. Over the next 75 minutes,
15 the light yellow, opaque solution was warmed to 45°C. After
stirring at this temperature for the next 18 hours, the
transparent polymer solution was poured into 200 ml of ice
and water in a blender. The resulting fibrous solid was
filtered and washed (in the blender) twice each with water
20 and ether. The product was dried in a vacuum oven at 15 mm
Hg pressure and 90°C for 18 hours. The polymeric product,
obtained in 92.2 % yield, was a very light-yellow fibrous
solid having the following recurring structural units:

25
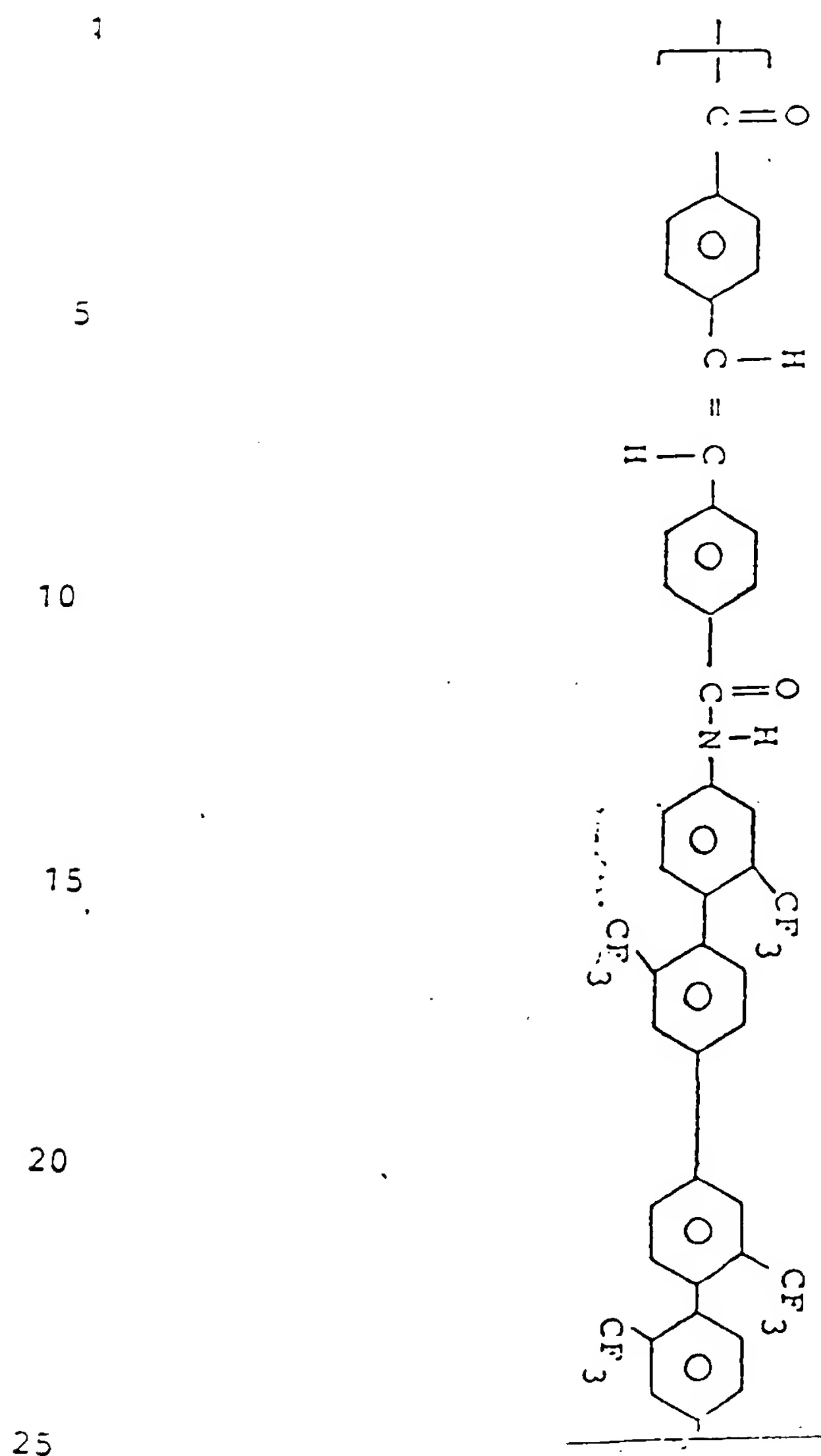
The inherent viscosity of a polymer solution (0.5 g of the polymer of Example 13 per 100 ml of a solution of 5 g lithium chloride per 100 ml of dimethylacetamide) was 1.31 dl/g at 30°C. The molecular structure of the polymer was confirmed by infrared spectroscopy. The polymer was

Elemental analysis for $C_{44}H_{24}F_{12}N_2O_2$ provided the following:

	%C	%H	%F	%N	%O
Calculated:	62.86	2.88	27.12	3.33	3.81
Found:	62.07	3.29	24.18	3.16	7.3 (by difference)

Thermogravimetric analysis showed that the onset of de-
gradation of the polymer of Example 13 occurred at 510°C in
nitrogen and at 440°C in air. Differential scanning calori-
metry and thermal mechanical analysis of film samples
detected a reproducible transition at about 187°C.

Polymeric films were prepared from the polymeric material
of Example 13 by casting (onto glass plates) solutions of
the polymeric material in a 5 % wt./vol. solution of lithium
chloride and dimethylacetamide (5 g lithium chloride per
100 ml of dimethylacetamide). The concentration of polymer
ranged from 0.5 to 5 % wt./vol., i.e., from 0.5 g to 5 g
polymer per 100 ml of the lithium chloride/dimethylacetamide
solution. In each instance, the glass plate carrying the
puddle-cast polymer solution was immersed in water (after
minimal evaporation of solvent). The polymer film was ob-
served to gel and a transparent and colourless unoriented
film separated from the glass plate. The resulting film was
soaked for several hours in water to effect extraction of
occluded lithium chloride and solvent, soaked in acetone and
dried in a vacuum oven at 90°C and 15 mm Hg pressure.
Refractive index, measured by interferometry, was 1.810.

Stretched polymeric films were prepared in the following
manner. Water-swollen films (obtained by soaking the polymer
films for several hours for removal of occluded lithium
chloride and solvent as aforedescribed) were cut into strips.

methanol and then in air at 220°C to effect film orientation.
The stretched films were optically transparent. Bire-

1 fringence, measured with the aid of a quartz wedge, was
0.87.

Example 14

5 This example illustrates the preparation of poly-[2,2',3",
2"'-tetrakis(trifluoromethyl)-1,1':4', 1":4", 1"'-4"'-
quaterphenylene] terephthalamide and the preparation there-
from of birefringent polymeric films.

10 A 100 ml reaction vessel (a resin-making kettle equipped
with a mechanical stirrer, nitrogen inlet tube and calcium
chloride drying tube) was heated while simultaneously
flushing the vessel with nitrogen. After the reaction
vessel had cooled to room temperature, 1.5 g of anhydrous
15 lithium chloride and 0.6301 g (0.001036 mole) of recrystall-
ized 4,4"'-diamino-2,2',3",2"'-tetrakis(trifluoromethyl)-
1,1':4',1";4",1"'-quaterphenyl were added while maintaining
a positive nitrogen pressure. The reaction vessel was fitted
with a thermometer and a rubber stopple and 10 ml of an-
20 hydrous distilled N-methylpyrrolidone (NMP) and 10 ml of
anhydrous distilled tetramethylurea (TMU) were carefully
added with the aid of syringes. The resulting mixture was
stirred and warmed to 40°C until all solids had dissolved.
The solution was then cooled in a bath of ice and salt to a
25 temperature of +5°C. A small amount of lithium chloride
precipitation was observed. Recrystallized terephthaloyl-
chloride (0.2103 g; 0.001036 mole) was carefully added by
means of a funnel to the stirred 2,2'-diaminoquaterphenyl
solution. An additional 10 ml of TMU, at a temperature of
30 10°C, were added through the funnel to the reaction mixture.
The temperature of the reaction mixture ....

thicken and streaming birefringence (but not stir
35 opalescence) was observed. Stirring was continued for an

1   The ice bath was removed from the reaction vessel, and when the temperature reached 27°C (in 30 minutes), the reaction solution had become very viscous. Over the next 75 minutes, the light yellow, transparent solution was warmed to 40°C. After stirring at this temperature for the next 18 hours,

5   the polymer solution was poured into 200 ml of ice and water in a blender. The resulting fibrous solid was filtered and washed (in the blender) twice each with water and ether. The product was dried in a vacuum oven at 15 mm Hg pressure and 90°C for 18 hours. The polymeric product, obtained in

10   93.5 % yield, was a white fibrous solid having the following recurring structural units:

15
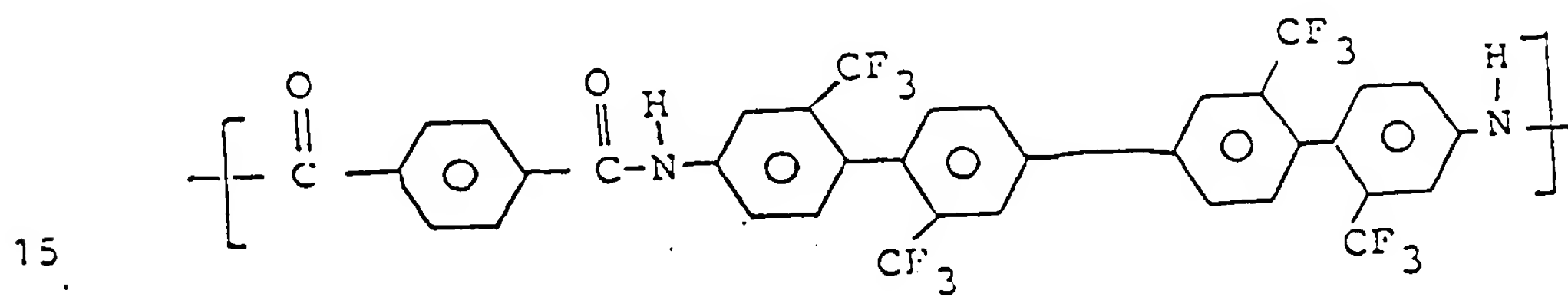
The inherent viscosity of a polymer solution (0.5 g of the polymer of Example 14 per 100 ml of a solution of 5 g

20   lithium chloride per 100 ml of dimethylacetamide) was 6.55 dl/g at 30°C. The molecular structure of the polymer was confirmed by infrared spectroscopy. The polymer was very slightly soluble in acetone, in tetrahydrofuran and in ethyl acetate and was soluble in amide-type solvents with

25   or without added lithium chloride.

Elemental analysis for $C_{36}H_{18}F_{12}N_2O_2$ provided the following:

%C	%H	%F	%N	%O

Thermogravimetric analysis showed that the onset of de-
composition of the polymer of Example 14 occurred at 440°C in
nitrogen.

thermal mechanical analysis of film samples detected a
reproducible transition at about 160°C.

Polymeric films were prepared from the polymeric material
of Example 13 by casting (onto glass plates) solutions of
the polymeric material in a 5 % wt./vol. solution of
lithium chloride and dimethylacetamide (5 g lithium
chloride per 100 ml of dimethylacetamide). The concentrat-
ion of polymer ranged from 0.5 to 5 % wt./vol., i.e. from
0.5 g to 5 g polymer per 100 ml of the lithium chloride/di-
methylacetamide solution. In each instance, the glass plate
carrying the puddle-cast polymer solution was immersed in
water (after minimal evaporation of solvent). The polymer
film was observed to gel and a transparent and colourless
unoriented film separated from the glass plate. The result-
ing film was soaked for several hours in water to effect
extraction of occluded lithium chloride and solvent, soaked
in acetone and dried in a vacuum oven at 90°C and 15 mm Hg
pressure. Refractive index, measured by interferometry,
was 1.79.

Stretched polymeric films were prepared in the following
manner. Water-swollen films (obtained by soaking the poly-
mer films for several hours for removal of occluded lithium
chloride and solvent as aforedescribed) were cut into
strips. The strips were mounted between the jaws of a
mechanical unidirectional stretcher. The strips were
stretched (in air at 220°C) to effect film orientation. The
stretched films were optically transparent. Birefringence,
measured with the aid of a quartz wedge, was 0.293.

Solutions of the polymer of Example 14 in lithium chl ...

of polymer is extruded into an aqueous coagulation bath for
gelling of the polymer material. The resulting transparent

1 colourless film strips were soaked in water and cut to
about 25.4 to 50.8 mm for testing. The partially oriented
strips of film produced by the extrusion were further
oriented by stretching in the manner described in the
Examples hereof. Measurement of birefringence itilizing a
5 quartz wedge provided a birefringence value of 0.44.

Example 15

Geometric indices were determined for the repeating units of
10 polymeric materials having the following structure

15
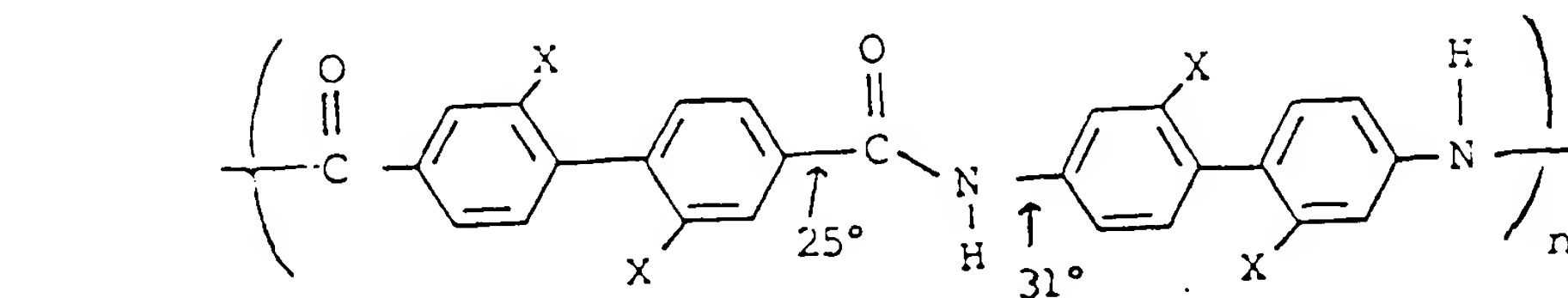
wherein each X is hydrogen or a substituent as set forth in
the following Table I. In the case of each recurring unit,
the eccentricity factor $\frac{1 + e_L}{1 + e_T}$ was calculated and is report-
20 ed in Table I. Bond and group polarizability tensors were
utilized to calculate a polarizability matrix for each
repeat unit, the diagonalized form of the matrix providing
the X, Y and Z contributions to the unit polarizability
ellipsoid. Axial polarizablilities, i.e., X, Y and Z, were
25 utilized to calculate longitudinal and transverse
eccentricities of each repeat unit, thus, reflecting its
symmetry.

eccentricity values were calculated utilizing the following

mer repeat unit. Literature values for polar-
ities are utilized from the literature, or where not avail-
able are constructed from bond polarizabilities. Available

1 Bond polarizabilities are utilized to connect segments
where necessary. To determine the overall polarizability
of the repeat unit, the coordinate system of the segment at
one end of the repeat unit os made coincident with that of
the adjacent segment by means of the appropriate rotat-
5 ion(s). This procedure is repeated on each successive
segment until the last segment is reached. Mathematically,
this means that the matrix of one segment must be pre- and
post-multiplied by a transformation matrix:

$$\alpha_1' = \underline{T} \; \alpha_1 \; T^{-1}$$

10

where α_1 is the polarizability of segment 1; $\underline{T}$ is the
transformation matrix; T^{-1} is the inverse of $\underline{T}$; and α_1' is
the polarizability of segment 1 in the coordinate system of
15 segment 2. The value of α_1' is then added to α_2 and the
transformation repeated. The repeat unit polarizability
matrix is diagonalized, thus, providing a repeat unit
polarizability ellipsoid with three semi-axes, i.e., α_{xx},
α_{yy}, and α_{zz}, where α_{xx} is the major polarizability and
20 is coincident with the polymer backbone.

Literature-reported values of 25° and 31°, respectively,
were utilized in all calculations as representing the di-
hedral angle betweeen the phenyl and carbonyl moieties and
25 the dihedral angle between the phenyl and amino moieties,
respectively, Experimentally determined values for the di-
hedral angle between each X-substituted phenyl moiety were
utilized in all calculations and are reported in Table I.
Mean diameter values, D, and length, L, were obtained from
30 spacefilling molecular models.

TABLE I

Substituent X (Dihedral Angle)	Mean Diameter (D)	Length (L)	$\left(\dfrac{1 + e_L}{1 + e_T}\right)$	G
H (20°)	4.49	21.35	1.061	0.989
F (60°)	4.61	21.35	1.206	1.21
Cl (72°)	4.78	21.35	1.348	1.23
Br (75°)	4.83	21.35	1.388	1.24
I (85°)	4.91	21.35	1.428	1.26
CF_3 (80°)	4.90	21.35	1.496	1.33
CH_3 (71°)	4.76	21.35	1.330	1.25

From the data presented in Table I will be observed the
influence of the nature of the X substituent relative to a
hydrogen atom as regards the reported dihedral angle and
resulting substantial noncoplanarity between interbonded
phenyl rings. Differences in mean diameter and influence of
the nature of X substituents on mean diameter and
eccentricity factor, and correspondingly, geometric index G
will also be observed. Thus, it will be noted that the
largest substituents, i.e., $-CF_3$ and $-I$ substituents,
corresponded with the largest dihedral angles between
interbonded phenyl groups or the hightest non-coplanarity
and, accordingly, recurring units having such substituents

For purposes of comparison, geometric index G was calculated
for the repeat unit of poly(p-phenylene)terephthalamide
having the following structure and the results thereof are

reported in Table II. Dihedral ange values of 25° and 31° were utilized for purposes of calculation as in the case of the repeat units of Example 15.
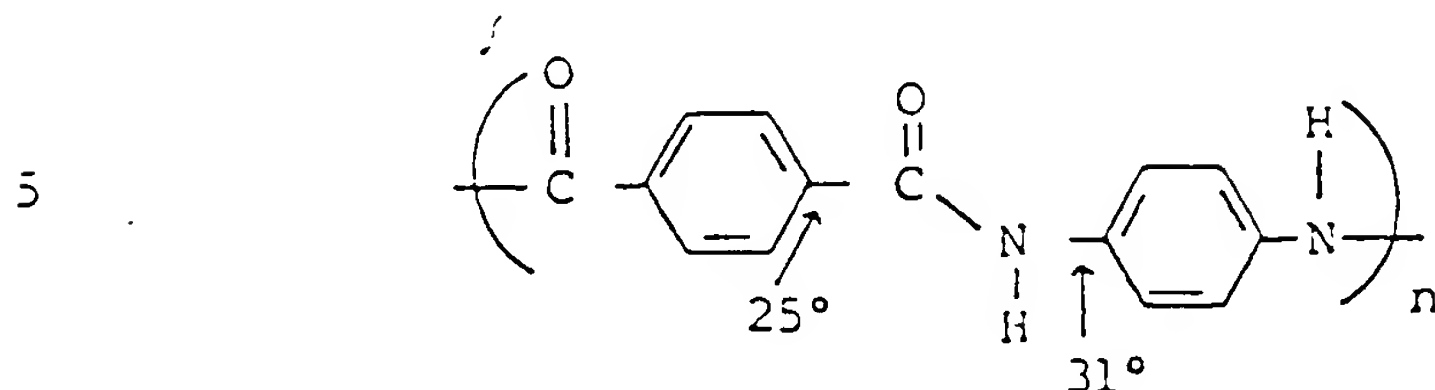

TABLE II

Mean Diameter (D)	Length (L)	$\dfrac{1 + e_L}{1 + e_T}$	G
4.43	12.45	0.978	0.621

As can be observed from inspection of the data reported in Tables I and II, the geometric indices for the repeat units og zhr materials set forth in Table I are considerably higher than the geometric index calculated for poly(p-phenylene)therephthalamide of Table II.

Example 16

Geometric indices for the recurring units of polyamides having the following structure were calculated. Each X sub-stituent was as indicated in Tabele III. Dihedral angles from the literature were utilized in such calculations. Calculated geometric indices were compared with values of theoretical maximum birefringence for the polymeric materials, reported in Table III. Theoretical maximum bi-refringence values (Δn_{max}) were obtained by plotting the
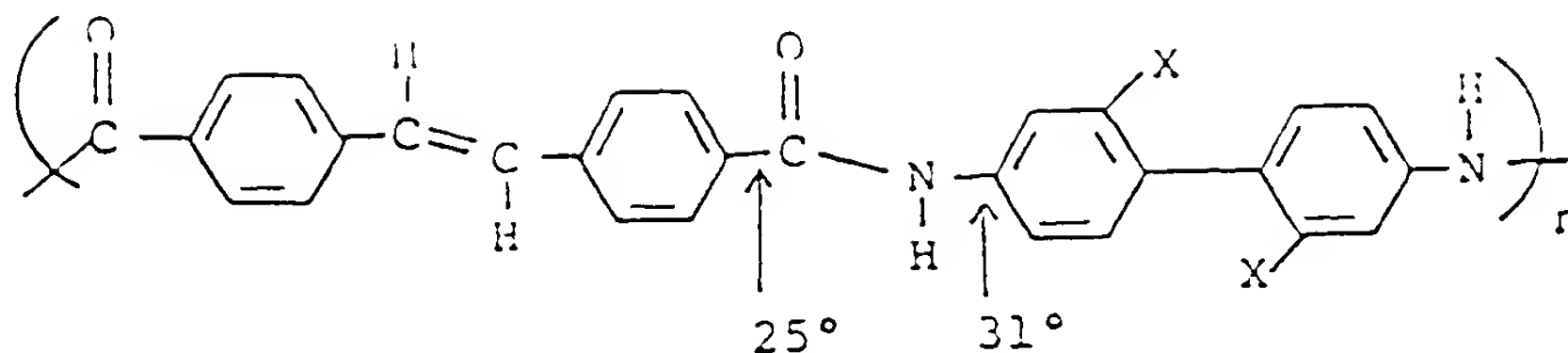
TABLE III

Substituent X (Dihedral Angle)	G	Δn_{max}
-Br (75°)	1.21	1.20
-CF$_3$ (80°)	1.18	0.98

From the data presented in Table III, it will be seen that high values of geometric index G corresponded with high values of Δn_{max}. For purposes of comparison, the theoretical maximum birefringence value (Δn_{max}) for the recurring unit of poly(p-phenylene)terephthalamide (having a G value of 0.621 as shown in Table II) was also determined. The resulting Δn_{max} value of 0.83 for poly(p-phenylene)terephthalamide was higher than would be predicted from the geometric index value, G, of 0.621. This is believed to be the result of the highly crystalline nature of the poly(p-phenylene)terephthalamide material, whereas the geometric index G reflects the inherent anisotropy of an isolated chain independent of such macroscopic properties as morphology, density, colour or the like.

rigid, rod-like uniaxial molecular structure of such materials and the amorphous/crystalline ratio thereof.

In the case of highly unidirectionally oriented phenyl-type polyamides this ratio generally will be in the range of about 0.3:1. The presence of crystallites is generally detrimental in polymeric materials adapted to utilization in optical devices owing to light scattering and diminished transparency. The non-coplanarity between substituted bi-phenyl rings, resulting from sterically bulky groups on the ortho positions of interbonded phenyl rings, raises the amorphous/crystalline ratio to a range of about 10:1 to about 20:1. This permits the fabrication of highly oriented films and fibres exhibiting high transparency in addition to high birefringence. The ring-substituted biphenyl poly-amides additionally exhibit enhanced solubility and can be fabricated into colour_less films or fibres where desired.

Example 17

Geometric indices were determined for the repeating units of polymeric materials having the following structure
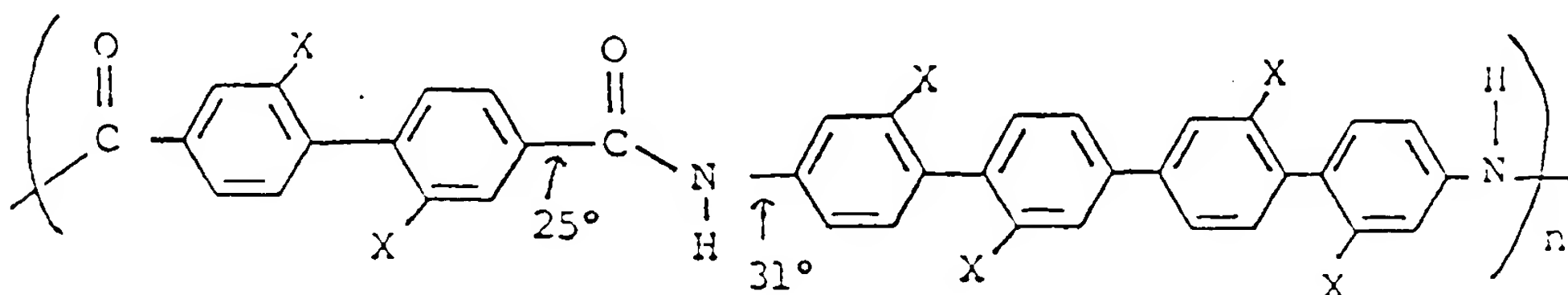
wherein each X is hydrogen or a substituent as set forth in the following Table IV. In the case of each recurring unit, the eccentricity factor $\dfrac{1 + e_L}{1 + e_T}$ was calculated and is

reported in Table IV. Bond and group polarizability matrix

polarizability ellipsoid. Axial polarizabilities, i.e., X, Y and Z, were utilized to calculate longitudinal and trans-

1 Eccentricity values were calculated utilizing the procedure set forth in Example 15.

Literature-reported values of 25° and 31°, respectively, were utilized in all calculations as representing the di-
5 hedral angle between the phenyl and carbonyl moieties and the dihedral angle between the phenyl and amino moieties, respectively. Experimentally determined values for the dihedral angle between each X-substituted phenyl moiety were utilized in all calculations and are reported in Table IV.
10 Mean diameter values, D, and length, L, were obtained from space-filling molecular models.

Table IV

Substituent X (Dihedral Angle)	Mean Diameter (D)	Length (L)	$\left(\dfrac{1 + e_L}{1 + e_T}\right)$	G
H (20°)	4.52	29.80	0.938	1.373
F (60°)	4.66	29.80	1.155	1.640
Cl (72°)	4.84	29.80	1.166	1.594
Br (75°)	4.90	29.80	1.145	1.546
I (85°)	4.99	29.80	1.271	1.685
CF_3 (80°)	4.98	29.80	1.286	1.708
CH_3 (71°)	4.82	29.80	1.181	1.621

hydrogen atom as regards the reported dihedral angle and resulting substantial noncoplanarity between interbonded

phenyl rings. Differences in mean diameter and influence of the nature of X substituents on mean diameter and eccentricity factor, and correspondingly, geometric index G will also be observed. Thus, it will be noted that the largest substituents, i.e., $-CF_3$ and -I substituents, corresponded with the largest dihedral angles between interbonded phenyl groups or the highest non-coplanarity and, accordingly, recurring units having such substituents show high geometric index values.

Example 18

A light-polarizing device utilizing a highly birefringent polyamide material was constructed in the following manner.

A sheet of birefringent material was prepared from the polyamide of Example 11, i.e., poly[2,2'-bis(trifluoro-methyl)-4,4'-biphenylene]-trans-p,p'-stilbene dicarboxamide. The sheet was prepared by the "wet-jet" extrusion method described in Example 11. The resulting extruded polymer, in the form of a partially oriented transparent colourless film, was soaked in water and cut into strips. The strips were then further oriented by stretching in air in the manner also described in Example 11. A strip of the birefringent polymer (having perpendicular and parallel indices of refraction, respectively, of approcimately 1.72 and 2.34 and an approximate thickness of 25μm) was embossed by con-tacting one surface of the strip with a brass prismatic plate heated to a temperature of 180°C and pressing the heated plate onto the surface of the film so as to provide a prismatic layer of birefringent material generally shown in Fig. 6 as layer 42.

approximately 1-mm thickness was poured a layer of poly-chlorinated biphenyl, an isotropic material having an index

1   of refraction of 1.654, available as Aroclor 1260 (R) from
Monsanto Company, St. Louis, Missouri. The prismatic layer
of birefringent material, prepared as aforesaid, was
placed onto the layer of Aroclor. The prismatic layer was
covered with a second layer of Aroclor so as to embed the
5   prismatic layer in Aroclor material. A second sheet of
glass was placed onto the Aroclor so as to sandwich the
birefringent and Aroclor materials between the two pieces
of glass. The resulting polarizer device was tested for
its light polarizing properties by placing the test device
10 and a second polarizer into the path of a light beam and by
observing the attenuation of light resulting from rotation
of the respective polarizers.

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20

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Claims

1. An optical device including a transparent molecularly oriented highly birefringent polymer, said highly birefringent polymer comprising repeating molecular units exhibiting high electron density substantially cylindrically distributed about the long axes of the polymer and the repeating units thereof, said highly birefringent polymer being substantially optically uniaxial exhibiting only two indices of refraction.

2. A device according to claim 1 wherein the birefringence of said polymer is in relation to the molecular configuration of said repeating molecular units and the cylindrical or ellipsoidal electron density distribution about said exes according to a dimensionless geometric index G represented by the relationship

$$G = 0.222 \times E \times \frac{L}{D}$$

wherein E is a dimensionless eccentricity factor defined by the relationship

$$E = \frac{1 + e_L}{1 + e_T}$$

where e_L is the longitudinal eccentricity of the electron polarizability of the repeating molecular unit and e_T is the transverse eccentricity of the polarizability of the repeating molecular unit, L is the length of the repeating molecular unit along the main axis thereof and D is the mean diameter of the repeating molecular unit and wherein

3. A device according to claim 2 wherein said geometric index G has a value of at least one, preferably at least 1.2.

1   4.   A device according to any preceding claim wherein said
molecularly oriented highly birefringent polymer has a bi-
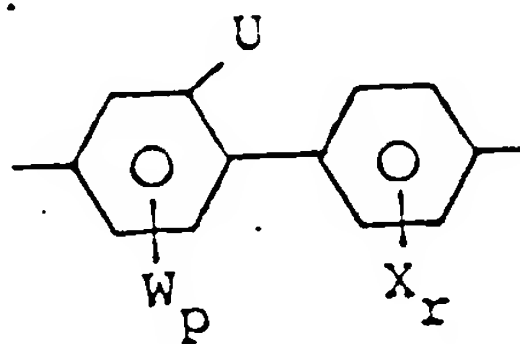refringence of at least 0.2, preferably at least 0.4.

5.   A device according to any preceding claim wherein said
5   molecularly oriented highly birefringent polymer is in the
form of a unidirectionally stretched polymer layer.

6.   A device according to claim 1 wherein said molecularly
oriented highly birefringent polymer comprises recurring
10   units of the formula

$$\left[\begin{matrix} O \\ \| \\ C \end{matrix} - A \left(\begin{matrix} O \\ \| \\ C \end{matrix} - \begin{matrix} R \\ | \\ N \end{matrix} - B \right)_c \begin{matrix} R^1 \\ | \\ N \end{matrix} \right] \quad ,$$
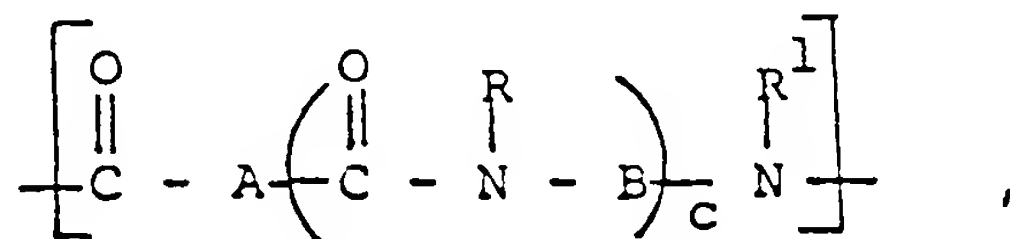
15   wherein each of A and B is a divalent radical except that B
can additionally represent a single bond; R and R^1 are
each hydrogen, alkyl, aryl, alkaryl or aralkyl; and c is
zero or one; and wherein, when c is one, at least one of
20   A and B is a divalent radical selected from the group con-
sisting of:

(1) a radical

where U is a substituent other than hydrogen, each W is
hydrogen or a substituent other than hydrogen, p is an

and Xr substitution being sufficient
radical with a non-coplanar molecular configuration; and

(2) a radical

$$-\text{(ring)}-\overset{Yt}{\underset{}{\bigcirc}}-\overset{Z}{C}=\overset{Z}{C}-\overset{Yt}{\underset{}{\bigcirc}}-$$

where each of Y and Z is hydrogen or a substituent other than hydrogen and each t is an integer from 1 to 4, with the proviso that when each said Z is hydrogen, at least one said Y substituent is a substituent other than hydrogen positioned on the corresponding nucleus ortho with respect

to the $-\overset{Z}{\underset{}{C}}=$ moiety of said radical, said Z and Yt substitution being sufficient to provide said radical with a non-coplanar molecular configuration;

and wherein, when c is zero, A is a divalent radical selected from the group consisting of radicals (1) and (2) as hereinbefore defined.

7.   A device according to claim 6 wherein c of said recurring units is the integer one.

8.   A device according to claims 6 or 7 wherein each said radical (1) is a divalent radical having the formula

$$-\text{(ring)}-\overset{U}{\underset{}{\bigcirc}}-\overset{}{\underset{X}{\bigcirc}}-$$
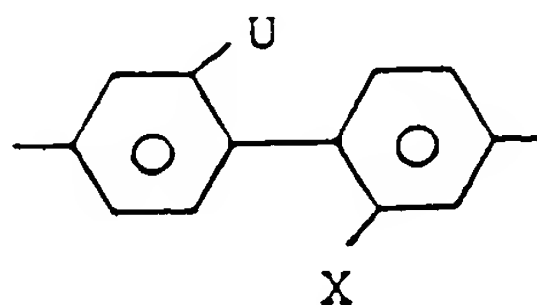
wherein each of U and X is a substituent other than hydrogen.

and X substituents is selected from the group consisting halogen, nitro, alkoxy and substituted-alkyl.

1   10.   A device according to claims 6 to 9 wherein each of
said A and B radicals of said recurring units is said di-
valent radical (1).

     11.   A device according to claim 10 wherein said divalent
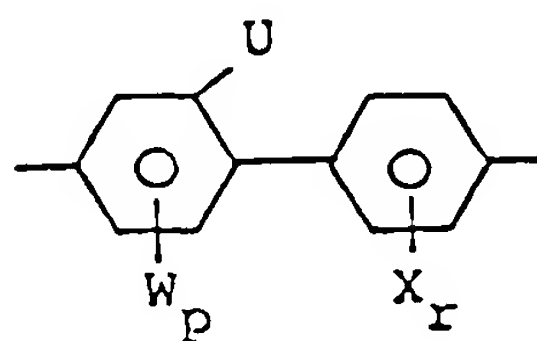5   radical A is a radical having the formula (1)
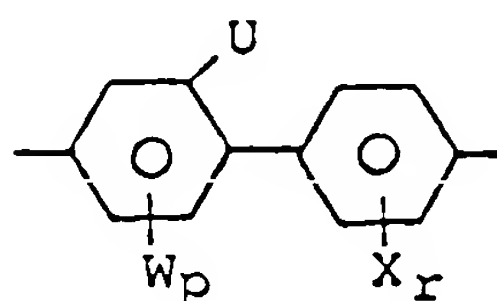
10

     wherein p is the integer 3, r is the integer 4 and each of U,
W and X is a substituent other than hydrogen, preferably a
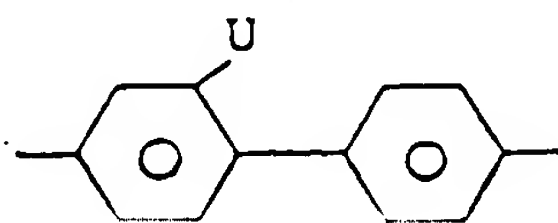halogen such as fluoro.

15

     12.   A device according to claim 10 wherein said divalent
radical A is a radical having the formula

20

     wherein p is the integer 3, r is the integer 4 and each of
25   U, W and X is a substituent other than hydrogen; and said
divalent radical B is a radical having the formula

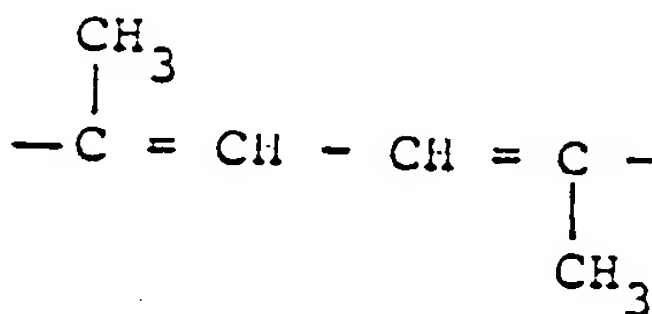   wherein each of U and X is a substituent other than
hydrogen.

13. A device according to claims 6 or 7 wherein said divalent radical A is the radical having the formula
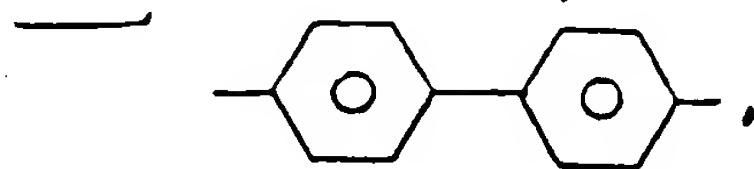
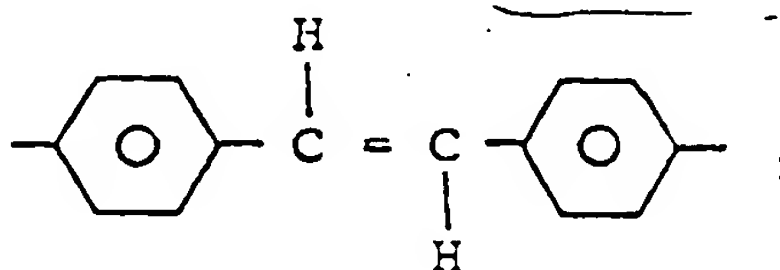14. A device according to claim 7 wherein said B represents a single bond.

15. A device according to claim 7 wherein said divalent radical A is the radical having the formula

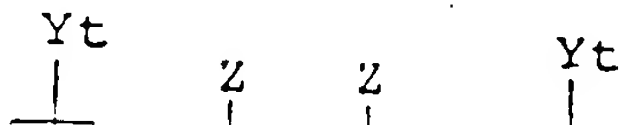$$-\overset{\overset{\displaystyle CH_3}{\displaystyle |}}{C} = CH - CH = \overset{\overset{\displaystyle |}{\displaystyle C}}{\underset{\displaystyle CH_3}{}} -$$

16. The device of claim 7 wherein said divalent radical A is the radical having the formula

17. A device according to claim 7 wherein at least one of said A and B radicals is said divalent radical having the formula

$$\overset{\overset{\displaystyle Yt}{\displaystyle |}}{} \quad \overset{\displaystyle Z}{\underset{\displaystyle |}{}} \quad \overset{\displaystyle Z}{\underset{\displaystyle |}{}} \quad \overset{\overset{\displaystyle Yt}{\displaystyle |}}{}$$
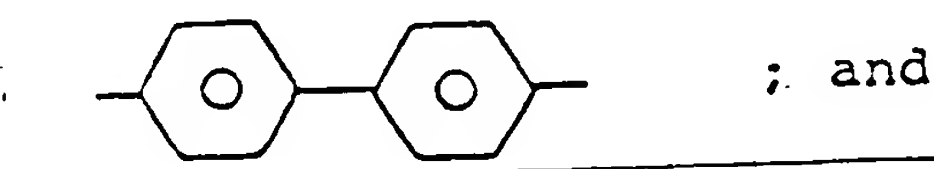
18. A device according to claim 17 wherein Z is hydrogen,

19. A device according to claim 18 wherein said Y substituent is selected from the group consisting of halogen, nitro and alkoxy.

20. A device according to claim 17 wherein each Y is hydrogen, each t is the integer four, one siad Z is hydrogen and the remaining said Z substituent is halogen.
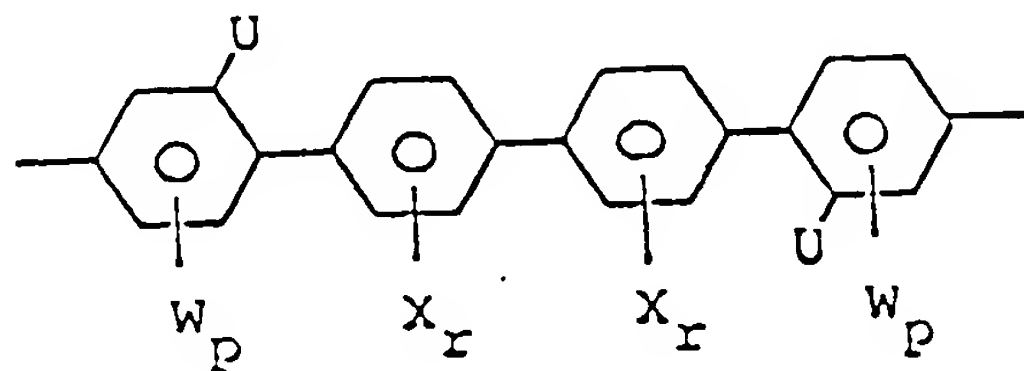
21. A device according to claim 6 wherein c is zero.

22. A device according to claim 7 wherein said divalent radical A is the radical having the formula

; and

said divalent radical B is a substituted-quaterphenylene radical having the formula

wherein each U is a substituent other than hydrogen, each W is hydrogen or a substituent other than hydrogen, each p is an integer from 1 to 3, each X is hydrogen or a substituent other than hydrogen and each r is an integer from 1 to 4, said U, W_p and X_r substitution being sufficient to provide said radical with a non-coplanar molecular con-

23. A device according to ...

radical A ist the radical having the formula

1 ation of bond and group polarizabilities of a repeating unit of a polymer. It will be appreciated that electron density distribution about axis X will be variously treated as a cylindrical or ellipsoidal distribution depending upon the relative magnitudes of the Y and Z vectors. In Fig. 4a is
5 shown an ellipsoidal cross-section along the axis of Fig. 3 where the magnitude of the shown Y vector is greater than that of the Z vector. Ideally, Y and Z vectors would be equal and the resulting circular cross-sectional distribution along the X axis is shown in Fig. 4b.
10

By a combination of longitudinal eccentricity (e_L) and transverse eccentricity (e_T), based upon bond and group polarizabilities, and the length and mean diameter of a repeating unit, a geometric index, G, related to optical
15 anisotropy or birefringence, can be represented as follows:

$$G = 0.222\left(\frac{1 + e_L}{1 + e_T}\right)\frac{L}{D}$$

20

wherein e_L, e_T, L and D have the meanings hereinbefore ascribed. Longitudinal eccentricity e_L may be represented according to the following relationship

25

$$e_L = \frac{\sqrt{X^2 - \frac{(Y + Z^2)}{2}}}{X}$$

Transverse eccentricity e_T may be represented by the

$$e_T = \frac{}{Y}$$

1 wherein the magnitude of vector Y is the larger of the Y
and Z vectors. Ideally, transverse eccentricity e_T will
equal zero and longitudinal eccentricty e_L will equal one,
in which case, eccentricity factor, E, will equal the
theoretical maximum of two.

5

Geometric index G can be calculated for a variety of re-
peating units of a polymer material by resort to mean
diameter and length values and longitudinal and transverse
eccentricity values calculated from experimentally determined
10 dihedral angles. It will be appreciated that the magnitude
of values of length, mean diameter, longitudinal eccentricity
and transverse eccentricity will materially influence the
value of geometric index G. Thus, it will be appreciated
that a repeating unit having, for example, a length of
15 about twice that of a repeating unit having a different
molecular structure and configuration will have a geometric
index of about twice that of such different repeating unit.
Accordingly, in making comparisons of geometric indices and
magnitude thereof in relation to structural differences
20 between comparative molecular repeating units, such differ-
ences in length should be borne in mind.

In general, experimentally determined values of birefringence
for polymeric materials comprised of repeating units as
25 aforedescribed will correlate directionally with values of
geometric index, G, of the repeating units. Thus, in general,
recurring units having higher geometric index values provide
polymers exhibiting higher birefringence. Polymeric materials
comprised of repeating units having a geometric index value,
of less 0.5 or higher exhibit high brefringence and can

comprising repeating units having geometric index values of
one or higher be utilized herein. Especially preferred
are polymeric materials comprising repeating units of geometric

1 transparent layers, each said additional transparent layer having an index of refraction substantially matching one of the two indices of refraction of each said layer of said molecularly oriented highly birefringent polymer.

5 30. A multilayer device according to claim 29 wherein each said additional transparent layer is isotropic.
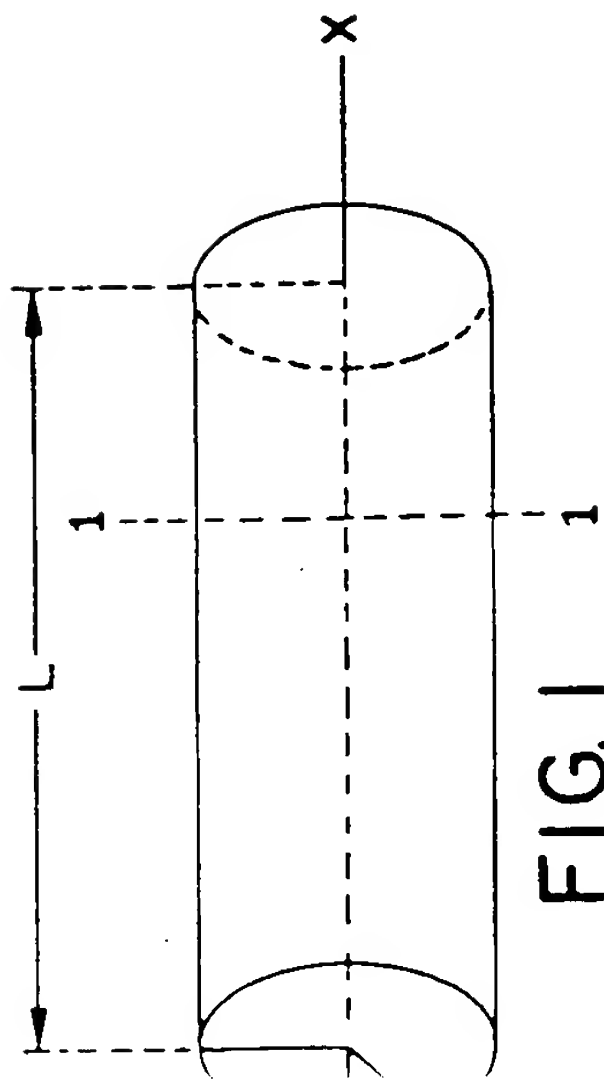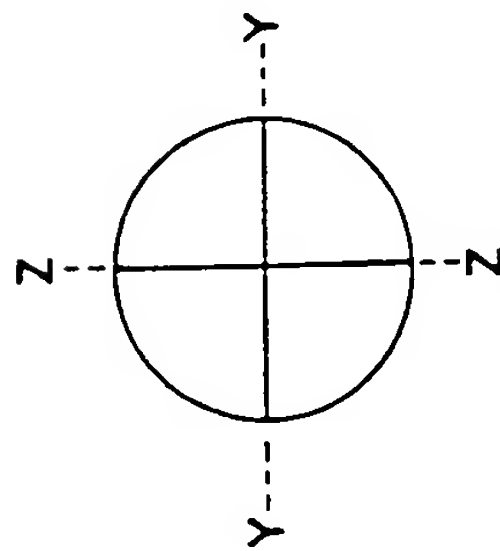
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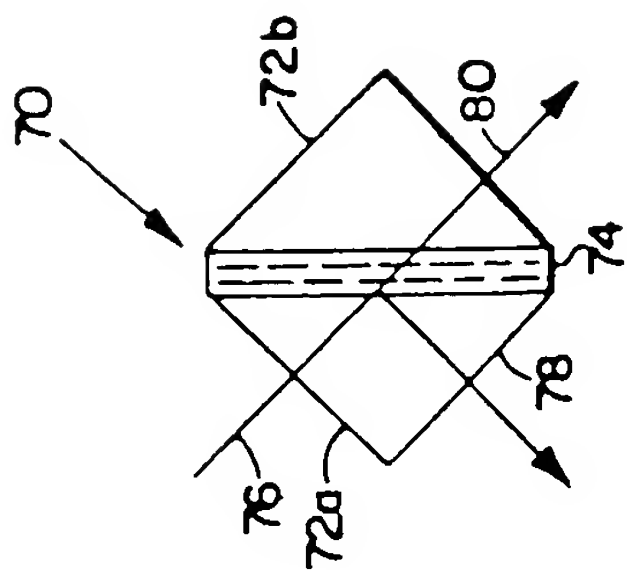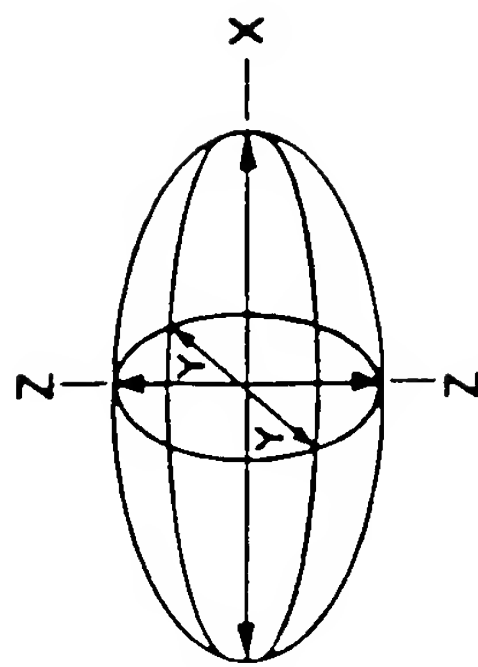25

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1/2

FIG. 8

FIG. 4b

FIG. 2

FIG. 4a

FIG. 1

FIG. 3

FIG. 5

FIG. 6

FIG. 7

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
Y	US - A - 2 451 695 (R.S. SCHREIBER) * claims 1, 5 to 7 * --	1,6
Y	GB - A - 1 011 836 (INTERNATIONAL POLA-ROID CORP.) * claims 1, 7, 9 * --	1,6
A	US - A - 3 801 528 (P.W. MORGAN) * claims; column 4, lines 35, 36 * --	6,17

A	Chemical Abstracts vol. 88 no. 4
	23 January 1978
	Columbus, Ohio, USA
	A.V. SIDOROVICH et al. "Quasicrystalline state of aromatic heterocyclic polymers with imide rings"
	page 9, column 2, abstract no. 23545n
	  & Dokl. Akad. Nauk.SSSR vol. 237, no. 1
	    1977, pages 156 to 159
	--	

D,Y	US - A - 3 610 729 (H.G. ROGERS) * claim 1; column 2, lines 50 to 65; fig. * --	1,5, 29,30
D,Y	US - A - 3 522 984 (H.G. ROGERS) * column 3, lines 62 to 74 * --	1,5

CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)

G 02 B   1/08
C 08 G 69/32

TECHNICAL FIELDS SEARCHED (Int.Cl. 3)

C 08 G 69/00
G 02 B   1/08
G 02 B   5/30

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
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A: technological background
O: non-written disclosure
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T: theory or principle underlying the invention
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X|

The present search report has been drawn up for all claims

  & member of the same patent family,

corresponding document

Place of search

EPO Form 1503   08.78
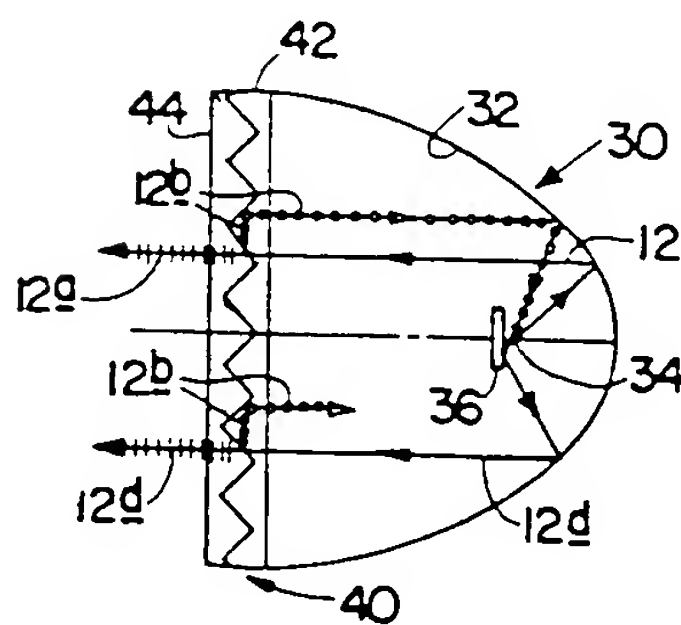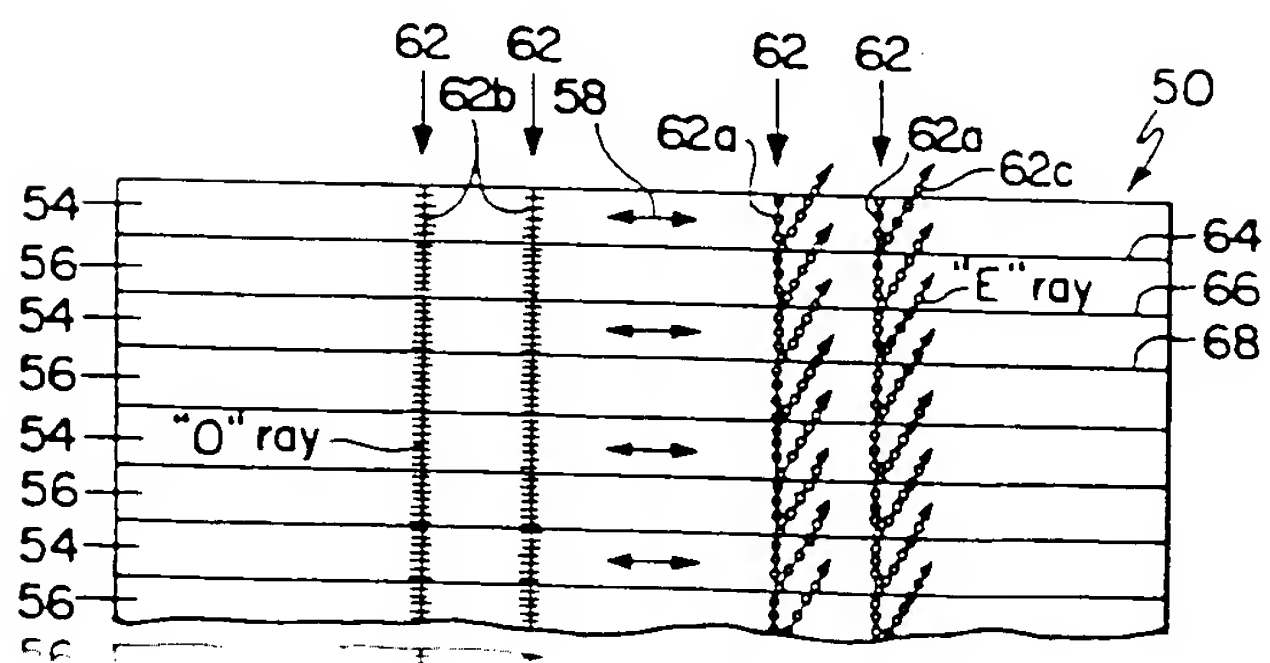
European Patent
Office

EUROPEAN SEARCH REPORT

Application number

EP 82 10 1572.4
- page 2 -

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.³)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
D,Y	US - A - 3 213 753 (H.G. ROGERS) * column 3, lines 8 to 28; column 9, line 74 to column 10, line 14 *	25-28	
A	DE - C - 732 790 (H. SCHNEIDER AG) * claim 1 *	1,5	
A	US - A - 2 748 659 (W. GEFFCKEN et al.) * fig. 1 * ----		TECHNICAL FIELDS SEARCHED (Int. Cl.³)